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FINAL REPORT

to

Jet Propulsion Laboratory

Pasadena, California

RESEARCH AND DEVELOPMENT STUDY ON THE RELATIONS BETWEEN VISCOSIMETRIC AND THERMODYNAMIC PROPERTIES OF MODERATELY CONCENTRATED POLYMER SOLUTIONS

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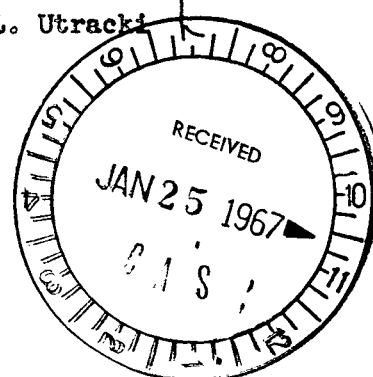


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SUMMARY

The object of this work was to study the relationship between the viscosimetric and thermodynamic properties of moderately concentrated solutions of vinyl aromatic polymers. The main effort under this Contract was to be directed toward the studies of the viscosity behavior of moderately concentrated solutions and to the extension of the proposed new method of generalization of polymer viscosity data into the range of higher concentration.

To attack the problems stated above we carried out both experimental and theoretical work. The first polymer studied experimentally was PAcN. Starting the measurements, we found it to be sensitive to light and temperature and unsuitable for viscosity measurements at higher concentrations. The observations and conclusions concerning this problem will appear in J. Polymer Sci., Polymer Letters, as a note entitled: On the Instability of Polyacenaphthalene in Solution. The original text of the note is enclosed as a part of this report.

After having made sure that the other polyvinyl aromatic samples were stable, we carried out the viscosity measurements of their benzene solutions at 30°C. The concentration range ($c \leq 4/[\eta]$ g/dl) was twice that mentioned in the original Statement of Work of the Contract, in order to achieve a more critical examination of the proposed method. The results, recently obtained, are summarized in the form of a preliminary manuscript entitled: Viscosity of Vinyl Aromatic Polymers. This concludes the requirements of paragraph (a)(1) and adds to the work stated in paragraph (a)(3) of the Statement of Work of the Contract.

The analysis of the applicability and extension to higher concentrations of previous articles (as required by paragraph (a)(2)) for 12 different polymer - solvent systems has been carried out and written up in the form of a paper entitled: Corresponding State Relations for the Newtonian Viscosity of Polymer

Solutions. Part II: Further Systems and Concentrated Solutions, which will appear in J. Polymer Sci., Polymer Phys. Series. It is enclosed as a part of the report. As can be seen, the proposed method gives good results for the concentration range up to 50% of polymer with the exception of low molecular weight polymer - very good solvent systems.

In order to better understand the proposed model of the interpretation of the viscosity behavior of polymer solutions, the literature data for the Huggins parameter for 46 systems were investigated, as reported in the last paper, entitled: Molecular Weight Dependence of the Huggins Constant k_1 and the Parameter γ . A semi-theoretical expression relating k_1 to molecular weight, coil permeability and the magnitude of polymer-solvent interactions was derived. On this basis an absolute scale for our proposed $\eta_{sp}/c[\eta]$ vs. c/γ plot was defined and a correlation obtained with the long range interaction parameter which defines the conformation of the macromolecule at infinite dilution.

ON THE INSTABILITY OF POLYACENAPHTHYLENE IN SOLUTION*

In the course of a study of the solution viscosities of vinyl aromatic polymers, we observed that the efflux times of polyacenaphthylene (PacN) in benzene and in dichloroethane (DCE) decrease with time, both during the experiments and while the solution is standing.

Attempts were made to find possible causes for such changes by measuring solution viscosities under various conditions and by investigating the influence of several additives. Supplementary measurements of IR, UV and FSR (1) spectra, gas-liquid chromatography (1) (GLC) and gel permeation chromatography (1) were also carried out.

During the preparation of this note, which is based on an internal report of our results in April, 1966, a paper by J. Springer, K. Ueberreiter and R. Wenzel (2) (SUW) appeared dealing with the photodecomposition of PacN in benzene. We shall examine the relationship between those and our findings later on.

The PacN samples used had been synthesized by thermal polymerization in bulk (1,3) and fractionated by the precipitation technique. Their properties are summarized in Table I. For the measurements we used the original samples, and those reprecipitated by adding an approximately 5% solution to MeOH. Before the measurements, the samples were dried at 50°C under vacuum for two weeks. Solvents were purified by washing, drying and distillation through a column prior to use. It took 3-5 hours to dissolve the polymer.

Viscosity measurements were carried out in Ubbelohde - type viscometers,

* This research was supported by the Jet Propulsion Laboratory, California Institute of Technology, under Study Project 951408.

using a Mechrolab auto-viscometer and constant temperature bath, the temperature being kept constant to $\pm 0.005^\circ\text{C}$ at 25 and 30°C . For the IR spectra, standard Perkin-Elmer Models 337 and 137 were used; for the UV - visible range, Carey 14 and Beckman instruments. The other data mentioned in this note were kindly supplied by the Stanford Research Institute and by the Jet Propulsion Laboratory (1).

Some of the results obtained for PAcN - benzene solutions at 25°C are shown in Fig. 1, curves 1 - 3, where the ratio $\eta_{sp}(t)/\eta_{sp}(t=0)$ is plotted as a function of time, t , (in min.). The rate of decrease of this ratio tends towards a constant value after the initial decrease. Even when the efflux time τ was measured during 5 to 6 days, it was still found to decrease at the same rate. The relative decrease in η_{sp} was found to be roughly proportional to the solution concentration.

Next the efflux times of benzene solutions of $c = 0.5$ g/dl were measured at 25°C under the following conditions: 1.) In viscometers with different capillary diameters, 2.) Under an atmosphere of dry air saturated with solvent vapor, 3.) In a conventional viscometer under normal- and a nitrogen atmosphere, 4.) After bubbling air through the solution, 5.) In the presence of water, 6.) During irradiation of the solution with a mercury lamp, and 7.) In a degassed solution in a sealed viscometer (1). In all these cases the efflux time decreases at the same rate as under normal conditions.

In a third set of measurements we checked the effects of temperature, light, and free radical scavengers. A comparison of curves 3 and 4 in Fig. 1 shows that the rate of decrease of τ is higher at the higher temperature. In Fig. 2 the typical $\tau(t)$ dependences are illustrated. It is found that heat, light and I_2 cause a sharp decrease of τ , however on returning to the initial condition the normal $\Delta\tau/\Delta t$ - value is assumed. On addition of other radical scavengers (anthraquinone, hydroquinone, DPPH), a different kind of behavior is noted. It is seen (Fig. 3) that in all these cases $\tau = \tau(t)$ passes through sharp maximums, and then in the presence of light τ decreases at the usual rate. In the absence of light,

however, the flow time becomes constant. A similar effect was found on addition of DPPH to a polystyrene - benzene solution (curve 3, Fig. 3).

In a separate set of experiments the changes in intrinsic viscosity of PACN - benzene solutions as a function of time and the influence of reprecipitation on $[\eta]$ were studied. Fig. 4 shows the results for the original sample F2, the once reprecipitated F2-1 and the twice reprecipitated F2-2. $[\eta]$ decreases after each reprecipitation (curves 1, 2a, 3a). After keeping samples at room temperature in the dark, the decrease in $[\eta]$ is the same, i.e. about 0.2% per day, regardless of whether the sample is kept in solution or in the solid form (curves 2b, 2c, 3b). Precipitation, followed by drying for two weeks at 50°C, results in a higher rate. M-data are listed in Table I.

In order to check for the presence of possible reaction products, a solution which was exposed to light for several weeks and had turned yellow in that time was examined by UV, IR, ESR and GLC methods. The IR spectrum of a film and the UV spectrum of the solution indicate the presence of acenaphthylene and acenaphthene. GLC measurements on the aged solution indicate the presence of oligomer - type products, although not of the monomer. From the ESR spectrum we can only conclude that the free radical concentration does not exceed 10^{15} sp/g of polymer.

Additional measurements were carried out in dichloroethane. In the course of a study of the relationship between $[\eta]$ and temperature, no significant changes in τ were observed at 25 and 35°C. However, at 45°C, τ was found to decrease logarithmically with time according to the expression: $-\Delta\tau/\Delta t = 1.21/t$, where the concentration of the solution equals 0.505 g/dl. Thus, in the DCE system, it was possible to reach an equilibrium state after sufficiently long periods. In Fig. 5 plots of η_{sp}/c vs. c are shown for 25°, 35° and 45°C. At 45°C the results change markedly after keeping the solution at that temperature for 3 days, at which point no further changes are noted. A decrease, both in $[\eta]$ from 0.546 to

0.518, and in the Huggins coefficient k_H from 0.95 to 0.50 are seen to have occurred.

Polyacenaphthylene is known to undergo degradation under various conditions, and studies have been reported on thermal (4,5), anionic (6) and recently also on photodegradation (2). Dilute solution properties of PAcN in several solvents, at or near room temperature have been studied (3,7,8) and although changes in properties have been noted (1-3), they were small and slow enough in these dilute systems to be ignored.

Our observations can be summarized by stating that changes in the solution viscosities are detectable even at low concentrations, the relative decrease in specific viscosity being roughly proportional to the solution concentration. With benzene as solvent, this decrease is not affected by the presence or absence of air and water, the rate of shear in the viscometer, or by far UV irradiation. It is, however, strongly accelerated by heat and by near UV and visible light. The change seems to take place even in the dark, at room temperature and in solid samples, although at a reduced rate. A comparison of the molecular weights and their distributions for each sample before and after reprecipitation (Table I) shows that the former decrease as a result of the reprecipitation treatment, in most cases by 20% or more, and that the molecular weight distribution tends to become broader. All this points to the existence of a degradation reaction in the PAcN samples, and on the available evidence a free - radical mechanism seems very likely. The slow decrease in viscosity and the relatively small changes in molecular weight suggest that this cannot be exclusively a random chain scission reaction. Also the presence of monomer and oligomers in the aged samples suggest that an unzipping process is at least partially responsible for the existing changes.

The acceleration of the degradation by iodine can be explained in terms of radical trapping, and thus of shifting a possibly existing degradation - recombination equilibrium in the direction of degradation, or alternatively by its action

as a free radical initiator. The latter possibility is in better accord with the fact that efficient radical scavengers like DPPH act in a completely different manner. (The occurrence of the same effect of DPPH in the polystyrene - benzene systems, shows that it is not specifically related to the phenomena associated with PAcN which we are discussing.)

In DCE, Fig. 4, the behavior is quite different. The change in $[\eta]$ and in k_H , as well as the existence of an equilibrium, indicate that both configurational and degradational changes may be occurring simultaneously. This difference could be due to the decreased solubility ($\theta = 35^\circ\text{C}$) and an enhanced possibility for chain transfer with the solvent. The transfer constants for benzene and DCE with styrene at 60°C are 1.8×10^{-6} and 3.2×10^{-5} respectively (11).

In qualitative accord with our results, SUW (2) also observe a viscosity decrease with time. They too find that the process is strongly accelerated by light, and dependent on wavelength, concentration and molecular weight. However, while in our samples and in the absence of light, a variation in $[\eta]$ of about 4% occurs in 25 days, their values of η_{sp}/c decrease by ca. 50% during the same time interval in solutions irradiated with a wavelength of 368 mμ. In daylight, at any rate, we observe a change in η_{sp}/c of about 0.5% per day.

The mechanism proposed by SUW is a photo - initiated preponderant random chain scission, as compared with our suggestion of a mixed chain scission - unzipping process. Another difference is found between the $[\eta]$ - M relations obtained in the two studies, namely: $[\eta]_{\text{SUW}} = 3.04 \times 10^{-4} M_n^{0.594}$ versus $[\eta]_{\text{JPL}} = 8.10 \times 10^{-5} M_w^{0.672}$, calculated by us.

While the difference in the apparent mechanisms of degradation can be explained by the different conditions of the reaction, the difference in the observed $[\eta]$ - M relations must be due to a different reason. Although this is not the main point of this work, we can speculate on possible reasons for these diver-

gent results. Assuming viscosities and osmotic pressures were obtained by SUW nearly simultaneously for a given sample, one may look for possible differences between the two sets of samples. They could reside in molecular weight distribution (MWD), stereoregularity (S), or branching. The two first causes can be readily rejected: MWD would require the heterogeneity to decrease with increasing M , or if $M_w/M_n = \text{const.}$ for all samples ($\text{const.} = 1.75$) $[\eta]$ for the lowest and highest M -samples would deviate in opposite directions more than 20%; S would demand a lower degree of stereoregularity for SUW. In Fig. 6, the JPL samples exhibit no differences related to their method of preparation, including solution polymerization, which if at all, should have resulted in a lower viscosity exponent. As for branching, there is no evidence in present results, but it would be compatible with the change in the viscosity exponent and the high conversions in SUW. Assuming $[\eta]_B = [\eta]_L$ for $M = 10^4$, which leads to $M_w/M_n \approx 2.5$ for the SUW samples, (see Fig. 6) and random branching with $n = 0.65$ (12) in the expression $[\eta]_B/[\eta]_L = g^n$, we can estimate a number of branches, viz. $f = 2$ and $f = 5$ for $M = 10^4$ and $M = 10^6$, respectively, (where $f = 1$ for a linear chain). In such a case the kinetic considerations would indicate long branches. If we further assume the existence of weak links at the branch points, it would follow that the main process in the SUW samples consists of a chopping off of the branches. This could lead to the kinetics found for the apparent random - chain scission process in the beginning (150-300 hrs.), and for the subsequent departures.

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Dr. J. Moacanin, at the Jet Propulsion Laboratory, Cal Tech, Pasadena, California. The gel permeation measurements were done by Dr. J. Heller at the Stanford Research Institute.

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TABLE I

Properties of PAcN Samples

Fraction	Treatment	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$	M_w/M_n	$A_2 \times 10^4$ (LS)	$R_G \times 10^4$ (LS)	$[\eta]_{25^\circ C}$ dl/g	$k_H, 25^\circ C$
FRVIII-F1	Original sample	3.24(LS)	2.33(OS)	1.39	0.94	795	1.82	0.43
F1-1	F1 reprecipitated	3.80(LS)	1.68(OS)	2.26	0.90	806		
F1a	F1, gel permeation*	3.24	2.33	1.39				
F1-1a	F1-1, gel permeation*	1.69	1.07	1.58				
FRVIII-F2	Original sample	1.85(LS)	1.44(OS)	1.28	0.97	535	1.37	0.41
F2-1	F2 reprecipitated	1.67(LS)	1.27(OS)	1.31	0.78	531	1.22	0.386
F2-2	F2-1 reprecipitated						1.02	0.465
F2a	F2, gel permeation*	1.19	0.87	1.37				
F2-1a	F2-1, gel permeation*	0.98	0.55	1.78				

* Gel permeation chromatography involves a residence time of the sample on the column of 2 hrs. at $70^\circ C$; sample F1 was used for calibration.

LEGENDS TO FIGURES

Fig. 1. Specific viscosity ratio of benzene solutions as a function of time. $\eta_{sp}(t=0)$ refers to the value immediately after the preparation of the solution.

Fig. 2. Effects of heat, light and iodine on efflux times, τ , of benzene solutions at 25°C; $c = 0.5$ g/dl.

1. Solution kept at 70°C between points shown by arrows. 2. Neon light switched on at point shown by arrow. 3. Iodine added to the solution at point shown by arrow.

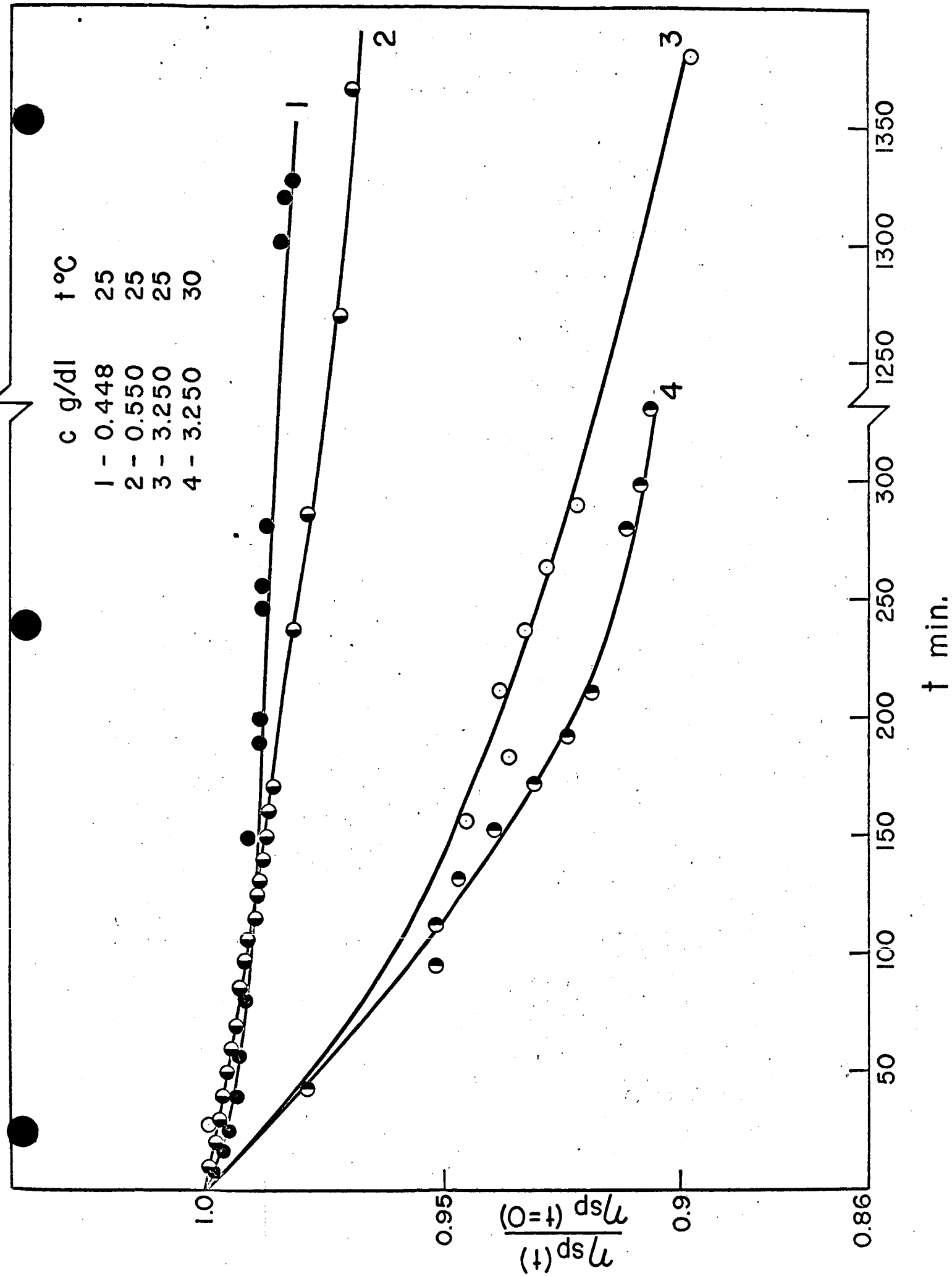
Fig. 3. Effect of radical scavengers on efflux time, τ , of benzene solutions at 25°C; $c = 0.5$ g/dl.

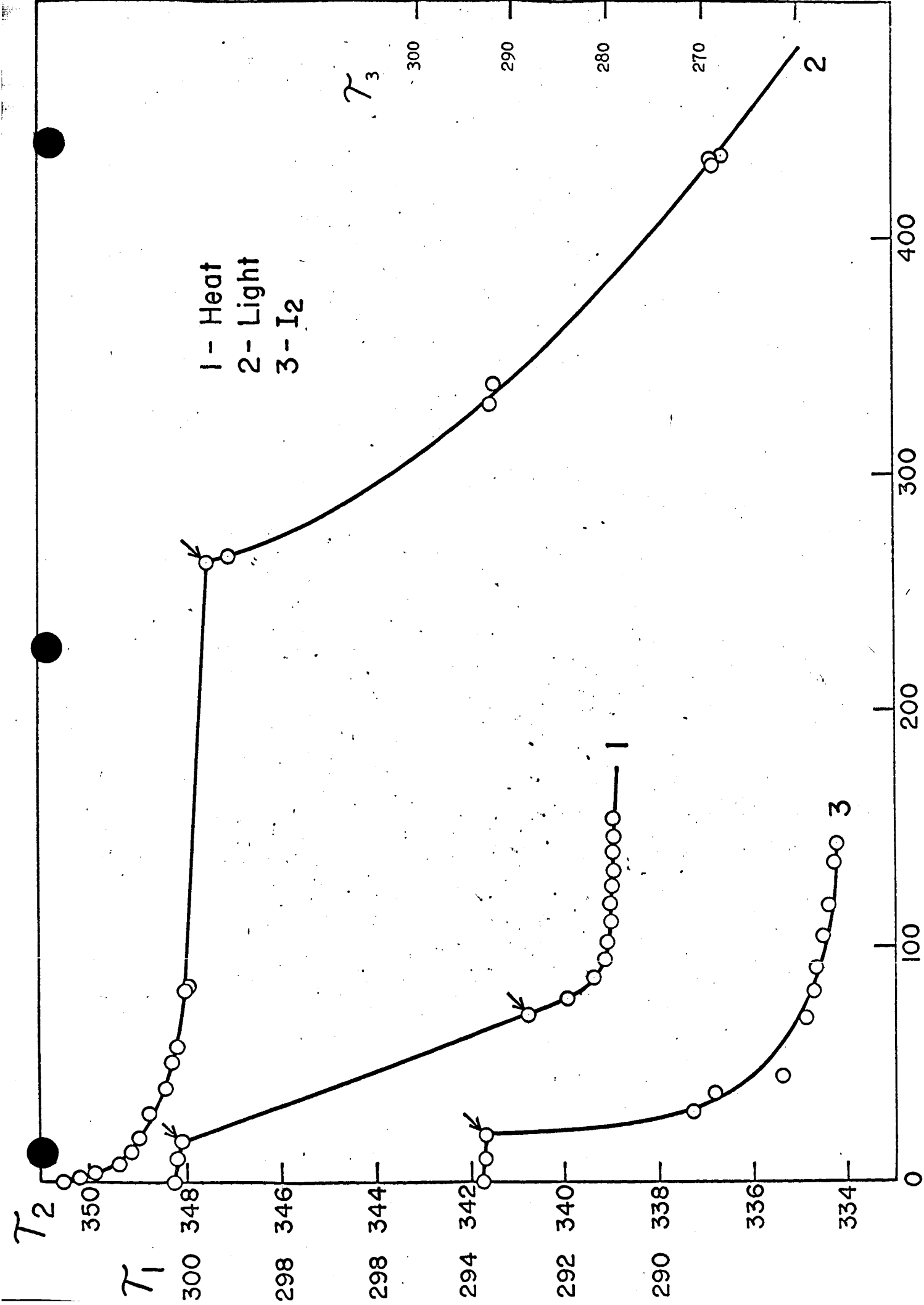
1. DPPH added to PAcN. 2. Anthraquinone added to PAcN. 3. DPPH added to polystyrene. The increase in τ in the initial and final part of this curve is due to solvent evaporation during the experiment.

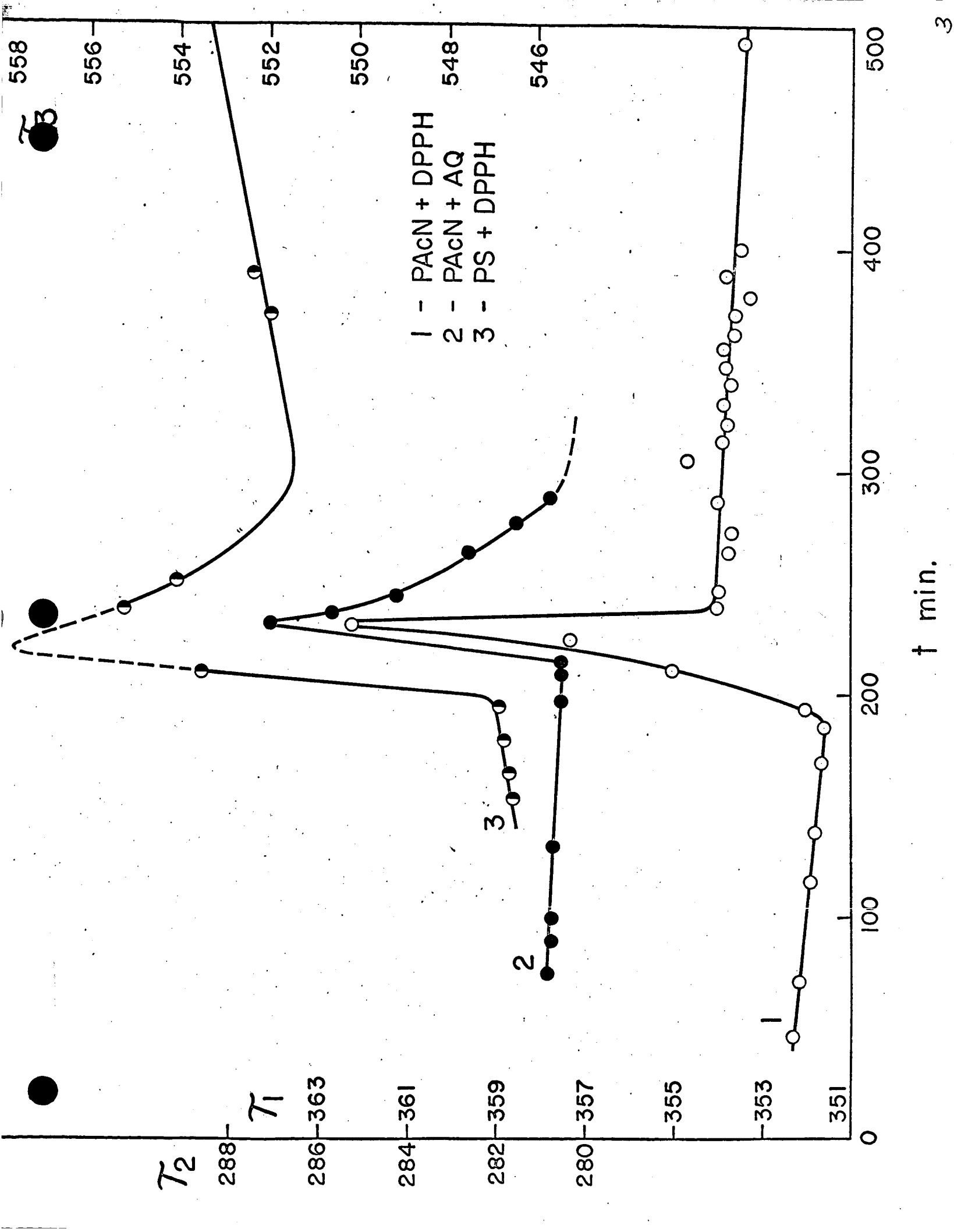
Fig. 4. Specific viscosity as a function of concentration for benzene solutions at 25°C. 1, 2a and 3a, samples F2, F2-1 and F2-2, see Table I. 2b and 3b, samples F2-1 and F2-2 measured after keeping in solution for 25 days. 2c, sample F2-1 after keeping in solid form for 25 days.

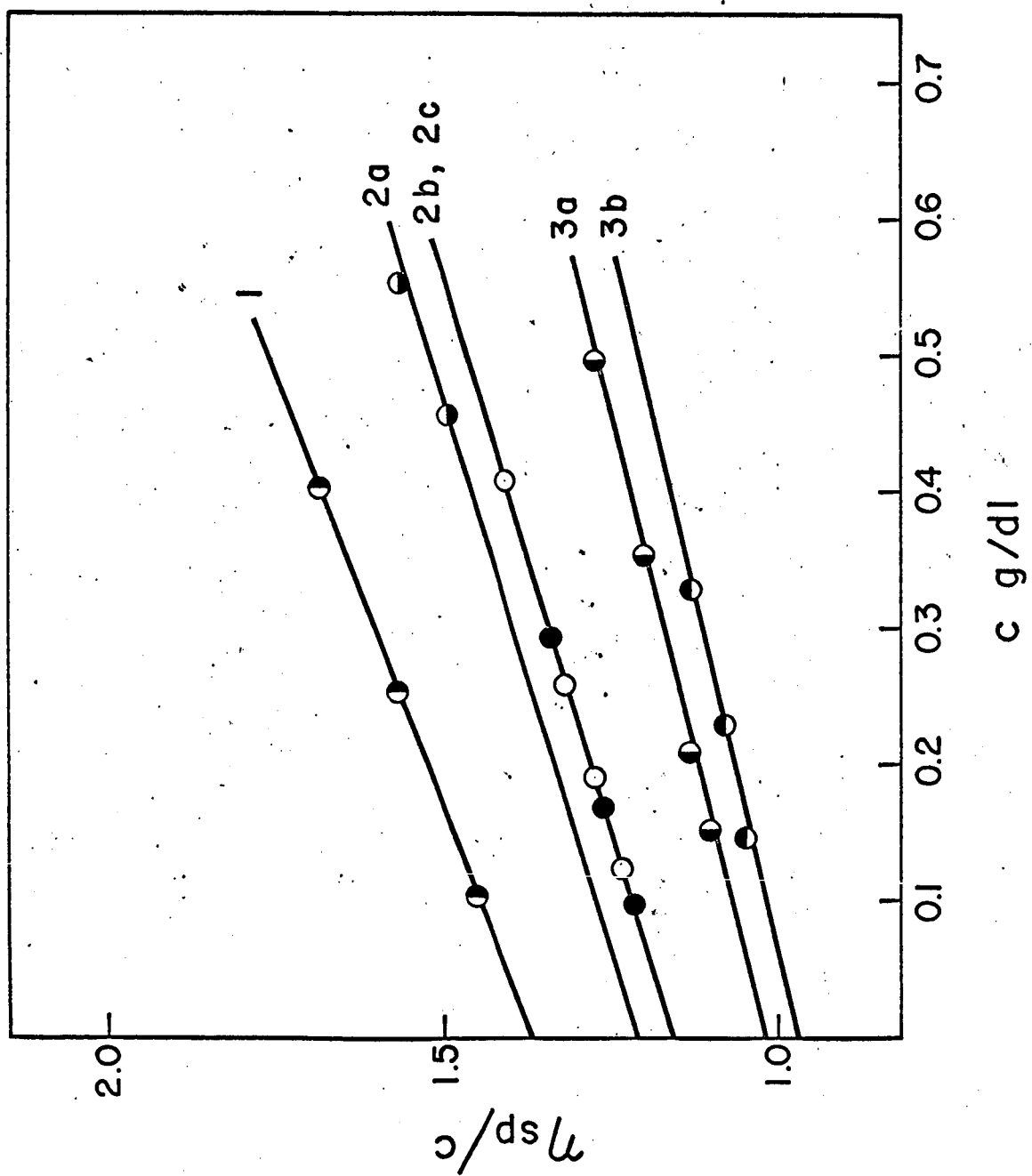
Fig. 5. Specific viscosity as a function of concentration for sample F2, see Table I, in dichloroethane, at various temperatures. Lowest curve, solution kept for 3 days at 45°C.

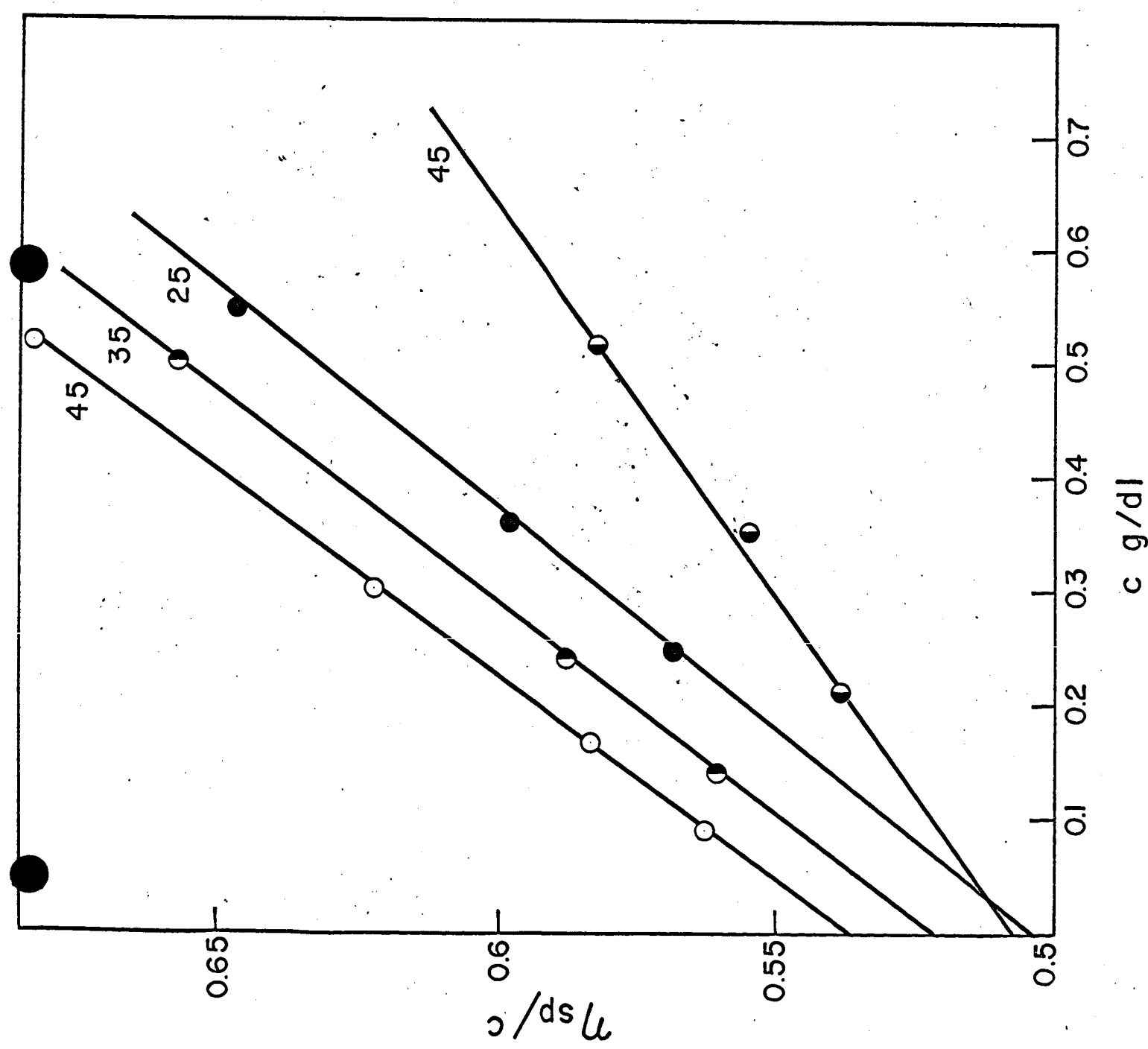
Fig. 6. Intrinsic viscosity - molecular weight relationship for benzene solutions at 25°C. Upper curve, number average, lower curve, weight average molecular weight.

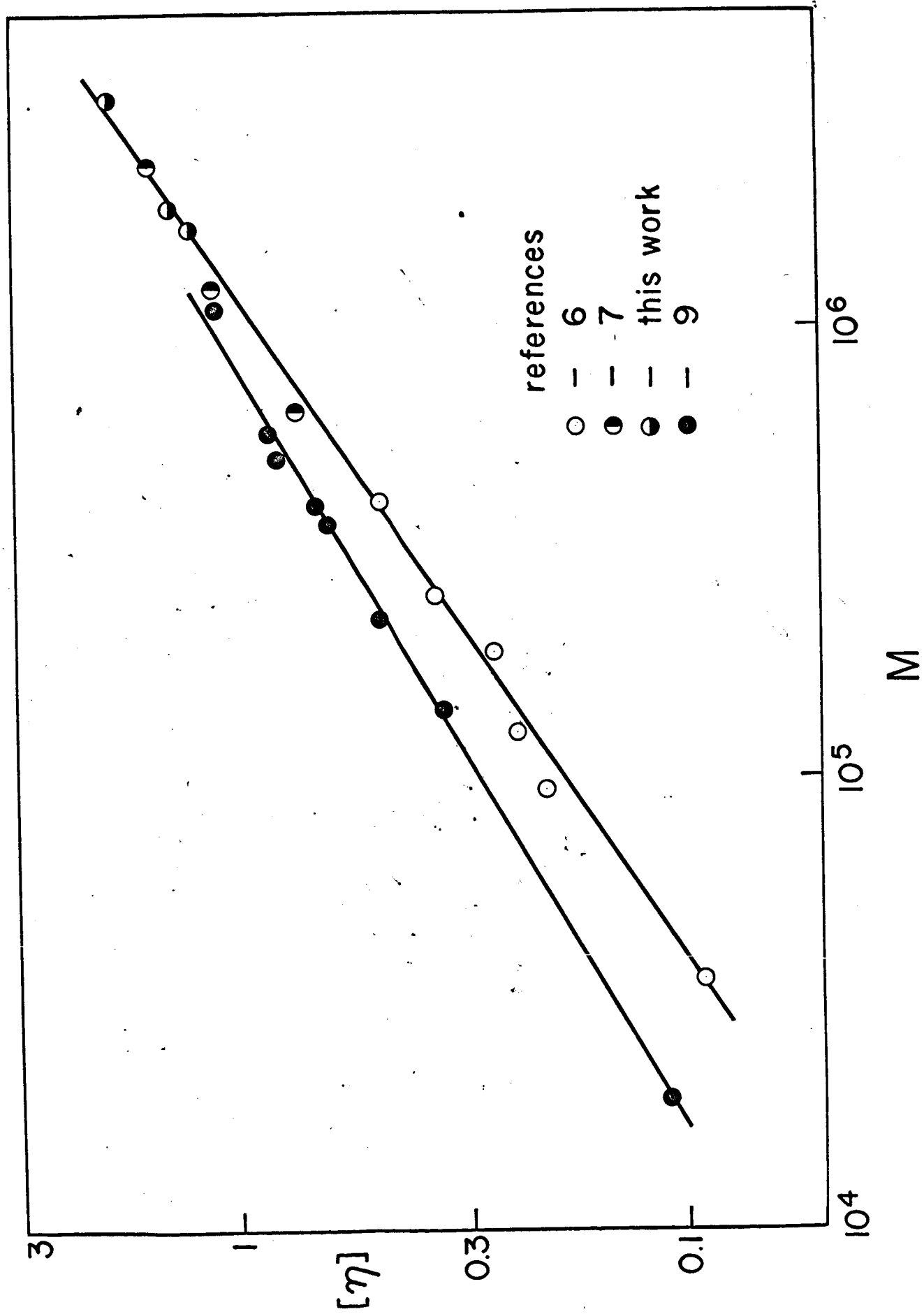












SOLUTION VISCOSITY OF VINYL AROMATIC POLYMERS

Introduction

It has been reported recently that the viscosity of polymer solutions can be expressed as a general function, independent of molecular weight (M);

$$\eta_{sp}/c[\eta] \equiv \tilde{\eta}(\tilde{c}) \quad (1)$$

where $\tilde{c} \equiv c/\gamma$, and the parameter $\gamma = \gamma(M, T)$ is characteristic of the polymer - solvent system, independent on concentration (c).

The above statement was first derived from analysis of η - c data of polystyrene (PS) solutions in θ solvents (¹), later found to hold for PS- near θ solvent systems (²) and very recently proven to be valid for polyisobutene (~~PIB~~), polyvinyl chloride (PVC), polyvinyl alcohol (~~PVA~~), cellulose derivatives (Cell.) and polyisoprene (~~PI~~) solutions (³). The viscosities for these 12 different polymer - solvent systems were measured in different laboratories, by different methods using samples of different heterogeneities. The proposed method of representing viscosity data gave very good results in the whole range of concentrations (up to 50%) for polymer-poor solvent systems. With increasing solvent power deviations in the lower molecular weight region were observed. These systems show similar deviations for $[\eta]$ - M and $[\eta]$ - T relations. For the PS-toluene system we observed deviations for samples with $M \leq 15,000$, for PIB-isooctane for $M \leq 20,000$, and for PVC-cyclohexane for $M \leq 26,000$.

In this paper we present c - η data for benzene solutions at 30°C of three vinyl aromatic polymers: poly-4-vinyl biphenyl (PVB), poly-1-vinyl naphthalene (P-1-VN), and poly-2-vinyl naphthalene, ^(P-2-VN) in the range of concentration $c \leq 4/[\eta]$ (g/dl). The c - η relations for these polymers can be directly compared with the PS-solvent systems. It is of particular interest to see how the increased bulk

of these aromatic side groups, and their various conformations would affect the polymer chain configuration and its solution behavior.

Experimental

prepared for JRL. (Dr J. Heller, et)

The polymers were kindly supplied by the Stanford Research Institute. They were prepared by anionic polymerization, fractionated and characterized by gel permeation chromatography (GPC) (4). PVB and P-2-VN samples were reprecipitated in our laboratory from benzene solution by MeOH and dried in a vacuum oven for two weeks at 50°C. Selected samples of these polymers measured before and after the precipitation showed no change in $[\eta]$ and in the Huggins constant k_1 . For P-1-VN we found that additional purification was not needed. The characteristics of all samples are presented in Table I.

Mallinckrodt's analytical reagent grade thiophene-free benzene further was purified by rectification on a packed column from over sodium wire. For all the experiments the middle fraction (B.P. = 80.0 - 80.1°C) ~~the middle fraction~~ from the same batch was used.

The polymer solutions were prepared one day before measurements in 10 ml volumetric flasks by heating the polymer-solvent mixture up to 50°C for ca. 30 min. Due to special care taken during the reprecipitation of polymer and the purification of the solvent, both components were dust-free and the solutions did not require filtration.

The viscosity measurements were carried out in a Hewlett-Packard Auto-viscometer Model 5901A with constant temperature bath Model 5901A, using Cannon-Ubbelohde dilution viscometers, calibrated by means of NBS-standard viscosity oils. The viscosimeter constants are shown in Table II. Kinetic energy and density corrections were applied to all individual measurements. We did not apply any correction for a rate of shear dependence. From Table II one can see that for all

systems $\beta \leq \beta_{\max} \approx \beta_{\text{crit.}}/10$, where $\beta_{\text{crit.}}$ is a generalized rate of shear above which $[\eta](\beta)$ starts to decrease; thus we should not expect any deviation due to shear stress in the region of infinite dilution. As far as the higher range of c and η is concerned we found that the viscosity of the same solution ($\eta \approx 1.5$ cp) measured either in viscometer 1 or 2 had the same value within the experimental error, which indicates the absence of shear stress influence in this region as well.

For each curve $\eta(M=\text{const.}) = \eta(c)$ four initial solutions were prepared in most cases.

The $[\eta]$'s were determined from highly diluted initial solutions. To calculate each $[\eta]$ value two methods were applied: 1) using the viscometer constants A and B (Table II) and the solution density we calculated the viscosity of each solution from its efflux time, τ . Using the solvent viscosity $\eta_0 = 0.564$ cp, a plot of η_{sp}/c vs. c was constructed. From this plot $[\eta]$ and k_1 were directly obtained. These values are shown in columns 2nd and 3rd in Table III. 2) The second way of calculating $[\eta]$ had been proposed by one of the authors (6): instead of applying the kinetic and density corrections to each individual τ value, the new set of constants $[\tau]$ and $k_{1\tau}$ ^{was} calculated from the $(\tau - \tau_0)/\tau_0 c$ vs. c plot (τ_0 is the efflux time of the solvent). From the values of $[\tau]$ and $k_{1\tau}$, $[\eta]$ and k_1 ^{were} ~~can be~~ calculated using the following equations:

$$[\eta] = [\tau](1+H)/(1-H) + D \quad (2)$$

$$k_1 = k_{1\tau}(1-H)/(1+H) - H(1-H)/(1+H)^2 + [\eta]D$$

where $H \equiv B/A\tau_0^2$ and $D = 10^{-2}(d_0^{-1} - d_p^{-1})$. As usual $[\eta]$ is expressed here in dl/g units, and d_0 and d_p are solvent and polymer densities in g/ml.

In columns 4 and 5 (Table III) the $[\tau]$ and $k_{1\tau}$ data are shown and in columns 6 and 7 $[\eta]$ and k_1 calculated from them by eq. (2). As can be seen, the agreement is quite good. The $[\eta]$ and k_1 data shown in Table I are the average values of

those shown in Table III.

Results

The η_{sp}/c values obtained for the three polymers are shown in Table IV. The $\tilde{\eta}$ values (eq. (1)) calculated from these data were plotted on a double logarithmic plot vs. c , and the curves obtained for the various M_w samples of each polymer were shifted along the c axis (1) to get the master-curve of $\tilde{\eta} = \tilde{\eta}(\tilde{c})$ as shown in Figs. 1-3. From these shifting procedures, values of the shifting parameter γ' were obtained, using one molecular weight as a reference, with $\gamma' = 1$. The γ' -values were converted to γ_2 -values through the relation (7) $\gamma_2 = \bar{K}\gamma'$, where \bar{K} is the average of $K^* = \gamma_1/\gamma'$ over all molecular weights for one polymer. The γ_1 -values were calculated from the separate set of lowest concentration viscosity data by means of the equation

$$\gamma_1 = \text{const.}/k_1[\eta] \quad (3)$$

where the value of the const. ³ for all systems ² was chosen as ¹ const. = 1.18. The \tilde{c} values shown in Figs. 1-3 are $\tilde{c} = c/\gamma_2$. The γ_1 and γ_2 values thus obtained are given in columns 8 and 9 of Table I, and are plotted against M_w in the inserts in Figs. 1-3. In the same figures, $[\eta]$ values are also shown as a function of M_w . From those insert plots the M dependence constants in the expressions

$$[\eta] = KM^a \quad (4a)$$

$$\gamma = K_1 M^{-a_1} \quad (4b)$$

were calculated. Their values are shown in Table V.

Discussion

From the $\tilde{\eta}$ against \tilde{c} plots shown in Figs. 1-3 it is clearly seen that the

proposed method for the superposition of η -c data is applicable to the three investigated polymers to varying degrees. Particularly, the data for PVB and P-2-VN, where the M-range is similar, show a very different behavior. For PVB, the $\tilde{\eta}$ vs. \tilde{c} data for samples of $M \leq 103,000$ deviate from the general curve, whereas for P-2-VN the data for all investigated samples with $M \geq 48,900$ can be superimposed. In the case of P-1-VN only a few samples in a narrow M-range were available, making a general statement about the behavior of this polymer very difficult. However, comparing samples with similar M-values of the three polymers it can be concluded that a deviation from the general relation is apparent for P-1-VN, though less pronounced than for PVB. Since the solvent, temperature, concentration range and the preparation, treatment and measurements of the solutions were the same in all cases, the observed difference can be ascribed only to differences in the conformations and configurations of the macromolecules in solution.

For a possible explanation of the varying applicability of the superposition treatment to these polymers, we look first at the interactions between solute and solvent molecules. It is generally accepted that the magnitudes of these interactions for vinyl polymers are related to the exponent a in eq. (4a) and increase of a is taken as an indication of increase of solvent power. It must be noted however, that a incorporates an effect of polymer conformation as well. The values of K and a , along with those of K_1 and a_1 (eq. (4b)) are shown in Table V. For comparison, Table V also includes the corresponding values for PS-cyclohexane at 34.4°C (θ -system) and for PS-toluene at 30°C (1).

Before proceeding any further, we would like to point out that the values listed in Table V for PVB, P-1-VN and P-2-VN were calculated by us from the $[\eta]$ and γ vs. M_w plots (see inserts in Figs. 1-3). The M_w values were determined by GPC, and the Q parameters relating elution distribution averages to M-averages were calibrated by light scattering and osmotic pressure data for several samples,

independently, for each of the three polymers (4). In all cases, the averages $Q_n \neq Q_w$ were found. In our opinion the M_w calculated from GPC, even if the numerical values of Q_w should not be correct, give a better relative set of values for all samples of the same polymer than would other methods. Thus, a possible error in Q_w may affect the K and K_1 values, but not those of a and a_1 . In Table V we are also showing the values of a and K listed in the literature. It can be seen that our a -values are the lowest in all cases. This can be explained partially by the fact that the density-correction in the calculation of $[\eta]$ is usually neglected, (this may account for an error of up to 5% in $[\eta]$ in the lower M region) and by the influence of M -heterogeneities of polymer samples.

It is seen that the a 's increase in the order P-2-VN - PVB - P-1-VN, which does not agree either with the order of the increasing deviations from the general $\bar{\eta}-\bar{c}$ relation nor with the increasing solubilities of polymers, namely P-2-VN - P-1-VN - PVB.

A more direct insight into the polymer-solvent interaction problem can be obtained by a separation of the short- and long-range interactions within the polymer chain, incorporated in $[\eta]$ and the second virial coefficient data. Two parameter theories (13,14) permit such separation according to the relations:

$$A_0 \equiv (\langle r_0^2 \rangle / N)^{1/2} \quad (5)$$

$$B \equiv (1/4 \pi^{3/2}) (N^2 \beta / 2M^2)$$

where N is the number of chain carbon atoms, and the other symbols have their usual meaning. From $[\eta]/M^{1/2}$ vs. $M^{1/2}$ plots, and assuming the Flory-constant

$\phi_0 = 2.87 \times 10^{-25}$, we calculated the values of A_0 and B shown in Table V. The corresponding values for PS-toluene at 25°C (13) are $A_0 = 0.986 \text{ \AA}$ and $B = 2.4 \times 10^{-27} \text{ ml}$. Other sources (15) give ^{an} even higher value (0.988 \AA) for the ^{effective length of the} statistical segment bond length of unperturbed atactic PS. It is interesting to note the following results:

1) The short and long range interaction parameters A_0 and B are of the same order of magnitude for PVB and PS-toluene solutions; 2) For P-1-VN the short range interaction parameter A_0 is comparatively smaller, but B is larger; 3) In contrast with P-1-VN, P-2-VN has the largest A_0 (the most extended coil) and at the same time a relatively small B, indicating weak interactions between solvent molecules and polymer segments.

The A_0 values decreasing in the order P-2-VN - PS - PVB - P-1-VN indicate a decrease in that order of the effective bond length, ~~i.e. intermolecular repulsion between neighboring segments~~. The parallel increase of B would thus point to increasing feasibility of segment-solvent competitive interaction. ~~Partially~~ P-2-VN molecules with the naphthalene rings sticking far out can easily interact among themselves, possibly in some fashion of stacking, to create extended rod-like structure, possibly of some helical character. In such structures, the number of sites available for polymer-solvent interactions is decreased, which lowers the value of the parameter B. In the case of P-1-VN, on the other hand, the freedom of movement of the naphthalene rings may be sterically hindered more strongly, preventing any kind of ordering of the side groups, i.e. preventing the formation of a highly-oriented chain conformation. Thus, segment-solvent interactions may be preferred, resulting in a more coiled structure and a higher B value.

To summarize, the order of increasing B-values ^(for the three investigated polymers) corresponds to the order of decreasing A_0 and simultaneously to the increasing values of the a -exponents. *Order of* Both a and B ^{values} differ from the order of the observed solubility and the applicability of the superposition method. This difference involves the reversal of position of PVB and P-1-VN. Due to the limited number of P-1-VN sample and the narrow M-range available and due to the large ~~probable~~ error in calculating B, we cannot decide whether this reversal is real, or results from an experimental error.

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LEGENDS TO FIGURES

Fig. 1. Reduced viscosity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for four samples of P-1-VN in benzene at 30°C. Insert; $[\eta]$, concentration reducing factor γ_2 and $\gamma_1 \equiv 1.18/k_1[\eta]$ as functions of M_w .

Fig. 2. Reduced viscosity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for six P-2-VN samples in benzene at 30°C. Insert; $[\eta]$, concentration reducing factor γ_2 and $\gamma_1 \equiv 1.18/k_1[\eta]$ as function of M_w .

Fig. 3. Reduced viscosity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for six PVB samples in benzene at 30°C. Insert; $[\eta]$, concentration reducing factor γ_2 and $\gamma_1 \equiv 1.18/k_1[\eta]$ as function of M_w .

Fig. 4. Summary semilogarithmic plot of reduced viscosity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for PS- θ solvent (curve 1), PS-toluene-30°C (curve 2), P-1-VN benzene - 30°C (curve 3), P-2-VN benzene - 30°C (curve 4), PVB-benzene - 30°C (curve 5) and PVC-cyclohexanone - 30°C (curve 6).

Fig. 5. Summary semilogarithmic plot of reduced viscosity $\tilde{\eta}$ as a function of new variable: $\tilde{c}_0 \equiv \tilde{c}\Lambda$. For explanation see text. The notation of curves is the same as in Fig. 4.

TABLE I
Characteristics of polymer samples.

No.	Symbol	$M_w \cdot 10^{-3}$	M_w/M_n	[η]*	Benzene	-	-	30°C	γ_2
					k_1^*	k_1	[η]	γ_1	
Poly-4-vinyl biphenyl									
1	8080-63-1	1,104.0	2.15	1.281	0.357	0.457	2.58	2.73	
2	8080-41-1	706.5	2.06	0.940	0.329	0.309	3.81	4.10	
3	8080-71-1	169.4	1.45	0.381	0.332	0.126	9.33	8.76	
4	8080-56-1	103.0	1.52	0.248	0.402	0.1005	11.74	12.38	
5	8080-51-1	80.8	1.26	0.234	0.364	0.0855	13.79	13.30	
6	8080-86-1	10.5**	—**	0.070	0.710	0.0497	23.74	22.12	
Poly-1-vinyl naphthalene									
1	8080-59-1	155.3	1.14	0.387	0.428	0.165	7.15	7.63	
2	8080-66-1	147.3	1.48	0.372	0.400	0.149	7.92	7.87	
3	8080-88-1	103.4	1.05	0.270	0.462	0.125	9.44	9.98	
4	8036-98	52.2	1.06	0.156	0.504	0.0788	14.97	12.91	
Poly-2-vinyl naphthalene									
1	8080-44-1	736.1	1.55	1.072	0.329	0.353	3.34	3.17	
2	8080-70-1	563.4	1.88	0.880	0.358	0.315	3.75	3.77	
3	8080-58-1	306.1	1.41	0.662	0.361	0.239	4.93	4.76	
4	8080-48-1	182.5	1.29	0.453	0.424	0.191	6.185	6.17	
5	8080-68-1	64.0	----	0.229	0.493	0.113	10.45	9.85	
6	8080-61-1	48.9	----	0.204	0.500	0.102	11.56	11.56	

* The average values from the data shown in TABLE III.

** ref. 4.

TABLE II

Characteristics of viscometers.

No.	Cannon Inst. Co. Symbol	A	B	$G_{\max} \cdot 10^{-3}/\text{sec}$	β_{\max}
1	D-707/50	0.0041543	1.425	1.48	0.0261
2	D-442/100	0.013718	2.60	0.89	0.0158

Constants A and B from the relation $v(c_{\text{st}}) = A\tau - B/\tau$, where τ is the efflux time in sec. G_{\max} and β_{\max} - maximum rate of shear and maximum generalized rate of shear: $\beta_{\max} \equiv ([\eta]\eta_0 M/RT)G_{\max}$ (η_0 is solvent viscosity).

TABLE III

[η] and k_L for vinyl aromatic polymers.

No.	[η] (from η)	k_L (from η)	[τ] (from τ)	$k_{L\tau}$ (from τ)	[η] eq.(2)	k_L eq.(2)
Poly-4-vinyl biphenyl						
1	1.282	0.359	1.247	0.375	1.280	0.355
2	0.940	0.317	0.914	0.362	0.939	0.342
3	0.380	0.360	0.370	0.325	0.383	0.304
4	0.250	0.384	0.237	0.445	0.246	0.420
5	0.235	0.362	0.224	0.389	0.233	0.366
6	0.071	0.860	0.064	0.588	0.069	0.559
Poly-1-vinyl naphthalene						
1	0.387	0.423	0.371	0.458	0.386	0.433
2	0.373	0.396	0.356	0.430	0.370	0.404
3	0.272	0.443	0.257	0.507	0.267	0.481
4	0.157	0.484	0.148	0.554	0.155	0.521

TABLE III (cont.)

[η] and k_1 for vinyl aromatic polymers.


No.	[η] (from η)	k_1 (from η)	[τ] (from τ)	$k_1 \tau$ (from τ)	[η] eq.(2)	k_1 eq.(2)
						
Poly-2-vinyl naphthalene						
1	1.072	0.322	1.041	0.360	1.073	0.335
2	0.880	0.368	0.854	0.370	0.880	0.349
3	0.663	0.359	0.639	0.387	0.660	0.364
4	0.453	0.420	0.433	0.453	0.448	0.429
5	0.230	0.495	0.219	0.519	0.228	0.491
6	0.206	0.496	0.194	0.531	0.203	0.504

TABLE IV

Viscosities of benzene solutions of vinyl aromatic polymers at 30°C.

No.	η_{sp}/c		η_{sp}/c		η_{sp}/c		η_{sp}/c		η_{sp}/c		η_{sp}/c	
	c g/dl	dL/g	c g/dl	dL/g	c g/dl	dL/g	c g/dl	dL/g	c g/dl	dL/g	c g/dl	dL/g
Poly-4-vinyl biphenyl												
M =			M = 80.8×10 ³		M = 103.0×10 ³		M = 169.4×10 ³		M = 706.5×10 ³		M = 1104.0×10 ³	
1	1.9661	0.07843	0.8694	0.2533	0.3356	0.2570	0.2938	0.3939	0.1124	0.9788	0.2004	1.4004
2	3.6604	0.08542	1.3468	0.2611	0.4677	0.2597	0.5534	0.4061	0.1506	0.9793	0.2952	1.4606
3	5.6546	0.09458	2.1921	0.2793	0.5034	0.2632	0.6761	0.4209	0.2333	1.0020	0.3571	1.4945
4	8.2120	0.1080	2.7695	0.2903	0.7085	0.2668	0.7555	0.4175	0.2979	1.0199	0.4385	1.5418
5	10.784	0.1250	3.0641	0.3014	0.8954	0.2690	0.9278	0.4256	0.4179	1.0547	0.5999	1.6391
6	15.205	0.1632	3.7148	0.3168	1.0643	0.2758	1.0358	0.4396	0.5268	1.0945	0.7587	1.7312
7	20.132	0.2287	4.6201	0.3436	1.3353	0.2827	1.4064	0.4597	0.7700	1.1814	0.9433	1.8400
8	25.901	0.3366	6.7231	0.4010	1.7087	0.3013	1.9226	0.4898	0.7846	1.1701	1.2186	2.0034
9	-----	-----	8.2061	0.4566	2.3518	0.3112	2.5449	0.5292	0.9993	1.1962	1.6907	2.3430
10	-----	-----	10.405	0.5502	3.0162	0.3295	3.3915	0.5582	1.2047	1.3169	1.8938	2.3819
11	-----	-----	13.391	0.7140	3.7920	0.3528	3.3918	0.5806	1.4943	1.3832	2.3155	2.6870
12	-----	-----	16.085	0.9289	4.9546	0.3917	4.7061	0.6519	1.7560	1.4828	2.4314	2.7877
13	-----	-----	19.089	1.2226	6.5424	0.4489	5.8178	0.7354	2.1459	1.7071	2.9928	3.2615
14	-----	-----	20.925	1.4872	6.6276	0.4519	6.6585	0.8030	2.3170	1.6572	3.6900	3.8596

TABLE IV (cont.)

Viscosities of benzene solutions of vinyl aromatic polymers at 30°C.

No.	η_{sp}/c		η_{sp}/c		η_{sp}/c		η_{sp}/c		η_{sp}/c	
	c	η_{sp}/c	c	η_{sp}/c	c	η_{sp}/c	c	η_{sp}/c	c	η_{sp}/c
	g/dl	dl/g	g/dl	dl/g	g/dl	dl/g	g/dl	dl/g	g/dl	dl/g
Poly-4-vinyl biphenyl (cont.)										
	$M =$	80.8×10^3	$M =$	103.0×10^3	$M =$	169.4×10^3	$M =$	706.5×10^3	$M =$	1104.0×10^3
15	-----	-----	-----	0.4837	6.6665	0.8092	2.9324	1.8582	4.0555	4.1615
16	-----	-----	-----	0.4998	7.8797	0.9635	3.5829	2.1038	5.0576	5.4463
17	-----	-----	-----	0.5739	9.2756	1.1982	3.7595	2.1671	-----	-----
18	-----	-----	-----	0.5787	9.4266	1.5152	4.6617	2.5349	-----	-----
19	-----	-----	-----	0.6995	11.513	-----	4.8344	2.6368	-----	-----
20	-----	-----	-----	0.8648	13.770	-----	5.9437	3.1292	-----	-----
21	-----	-----	-----	1.1044	16.598	-----	6.1664	3.3310	-----	-----
22	-----	-----	-----	-----	-----	-----	8.1869	4.4842	-----	-----
23	-----	-----	-----	-----	-----	-----	11.123	7.4864	-----	-----
Poly-1-vinyl naphthalene										
	$M =$	52,200	$M =$	103,400	$M =$	147,300	$M =$	155,300		
1	0.4380	0.1628	0.3221	0.2822	0.3514	0.3906	0.5009	0.4196		
2	0.5475	0.1640	0.4920	0.2878	0.4838	0.3987	0.7927	0.4375		
3	0.7181	0.1669	0.7170	0.2947	0.6594	0.4083	1.2896	0.4689		

TABLE IV (cont.)

Viscosities of benzene solutions of vinyl aromatic polymers at 30°C.

No.	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g
Poly-1-vinyl naphthalene (cont.)										
	M = 147,300									
18							7.5586	0.9247		
19							8.6027	1.0350		
20							8.9162	1.1295		
21							11.4176	1.4566		
22							15.4140	2.3697		
Poly-2-vinyl naphthalene										
	M = 59,600									
1	0.6245	0.2464	0.6440	0.2192	0.3493	0.4834	0.2374	0.7046	0.2537	0.95118
2	0.7780	0.2505	0.9056	0.2243	0.6036	0.5040	0.4482	0.7335	0.4242	1.0004
3	1.2298	0.2624	1.3221	0.2326	0.8422	0.5297	0.6437	0.7656	0.5228	1.0358
4	1.6069	0.2705	1.7840	0.2419	0.8969	0.5314	0.6984	0.7594	0.6217	1.0598
5	1.6700	0.2728	2.4546	0.2545	1.1554	0.5578	0.8636	0.8007	0.7802	1.1096
6	2.0461	0.2834	3.2498	0.2725	1.2098	0.5560	1.0313	0.8140	0.8832	1.1235
7	2.7347	0.3001	4.3922	0.3031	1.3954	0.5800	1.2415	0.8590	1.1362	1.2092
8	3.7563	0.3366	5.9305	0.3373	1.9615	0.6317	1.2629	0.8538	1.6620	1.3687
	M = 182,000									
	M = 346,000									
	M = 525,000									
	M = 736,000									
1	0.6245	0.2464	0.6440	0.2192	0.3493	0.4834	0.2374	0.7046	0.2537	0.95118
2	0.7780	0.2505	0.9056	0.2243	0.6036	0.5040	0.4482	0.7335	0.4242	1.0004
3	1.2298	0.2624	1.3221	0.2326	0.8422	0.5297	0.6437	0.7656	0.5228	1.0358
4	1.6069	0.2705	1.7840	0.2419	0.8969	0.5314	0.6984	0.7594	0.6217	1.0598
5	1.6700	0.2728	2.4546	0.2545	1.1554	0.5578	0.8636	0.8007	0.7802	1.1096
6	2.0461	0.2834	3.2498	0.2725	1.2098	0.5560	1.0313	0.8140	0.8832	1.1235
7	2.7347	0.3001	4.3922	0.3031	1.3954	0.5800	1.2415	0.8590	1.1362	1.2092
8	3.7563	0.3366	5.9305	0.3373	1.9615	0.6317	1.2629	0.8538	1.6620	1.3687

Viscosities of benzene solutions of vinyl aromatic polymers at 30°C.

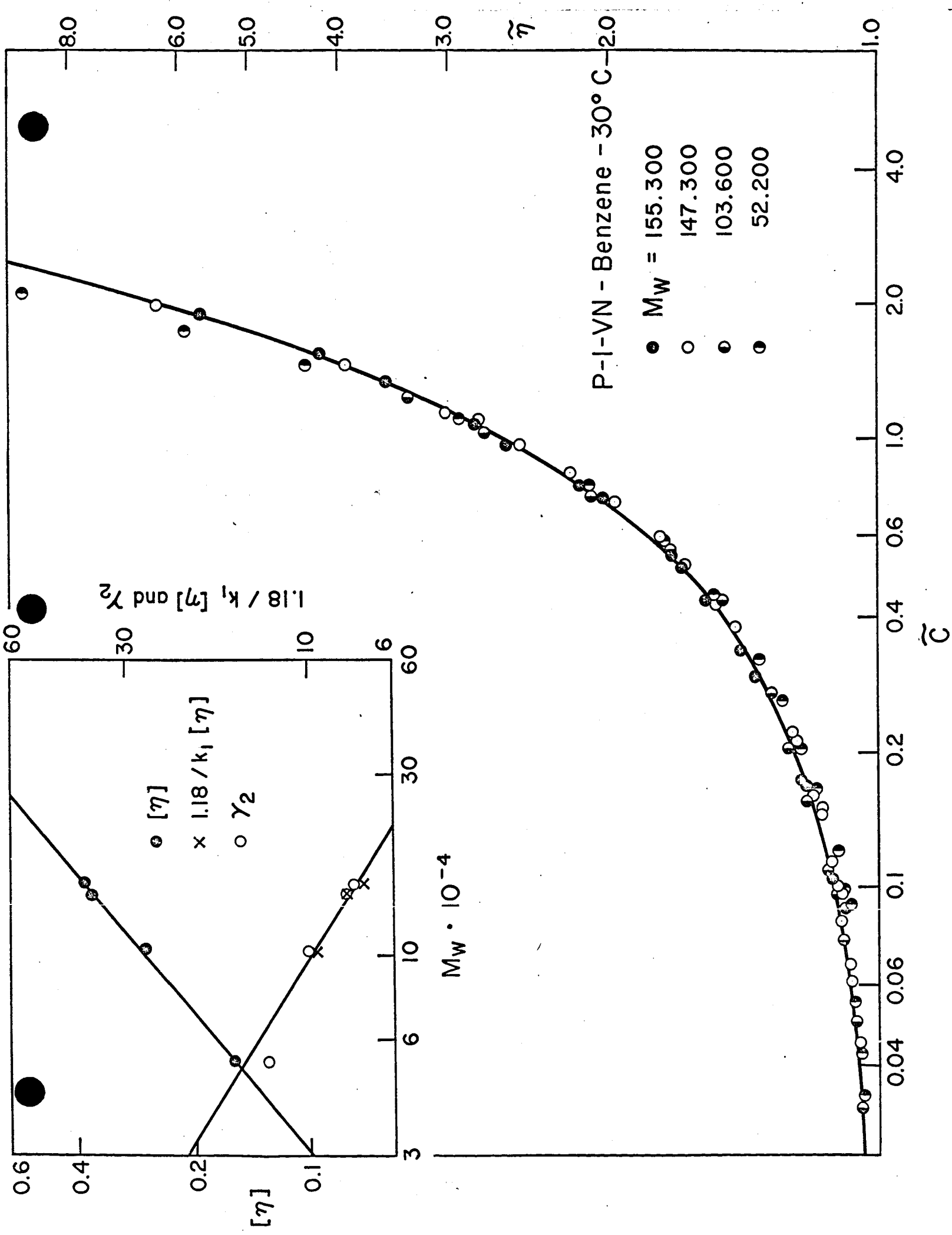
No.	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g
Poly-2-vinyl naphthalene (cont.)										
	M = 59,600		M = 115,600		M = 182,000		M = 346,000		M = 525,000	
9	5.0589	0.3703	10.3337	0.4235	2.8604 0.6980	1.7091	0.9317	2.4275	1.5826	1.5927
10			14.4978	0.5946	2.8604	0.7103	2.5170	2.7593	1.6704	1.5927
11					4.1921	0.8472	2.5843	3.5225	2.0179	2.2547
12					6.3111	1.1438	3.0786	4.4374	2.3503	3.0611
13					10.3952	1.8522	3.7891	5.4777	2.9102	4.2072
14							4.6772	5.9243		4.6467
15							5.7134			
16							9.3102			

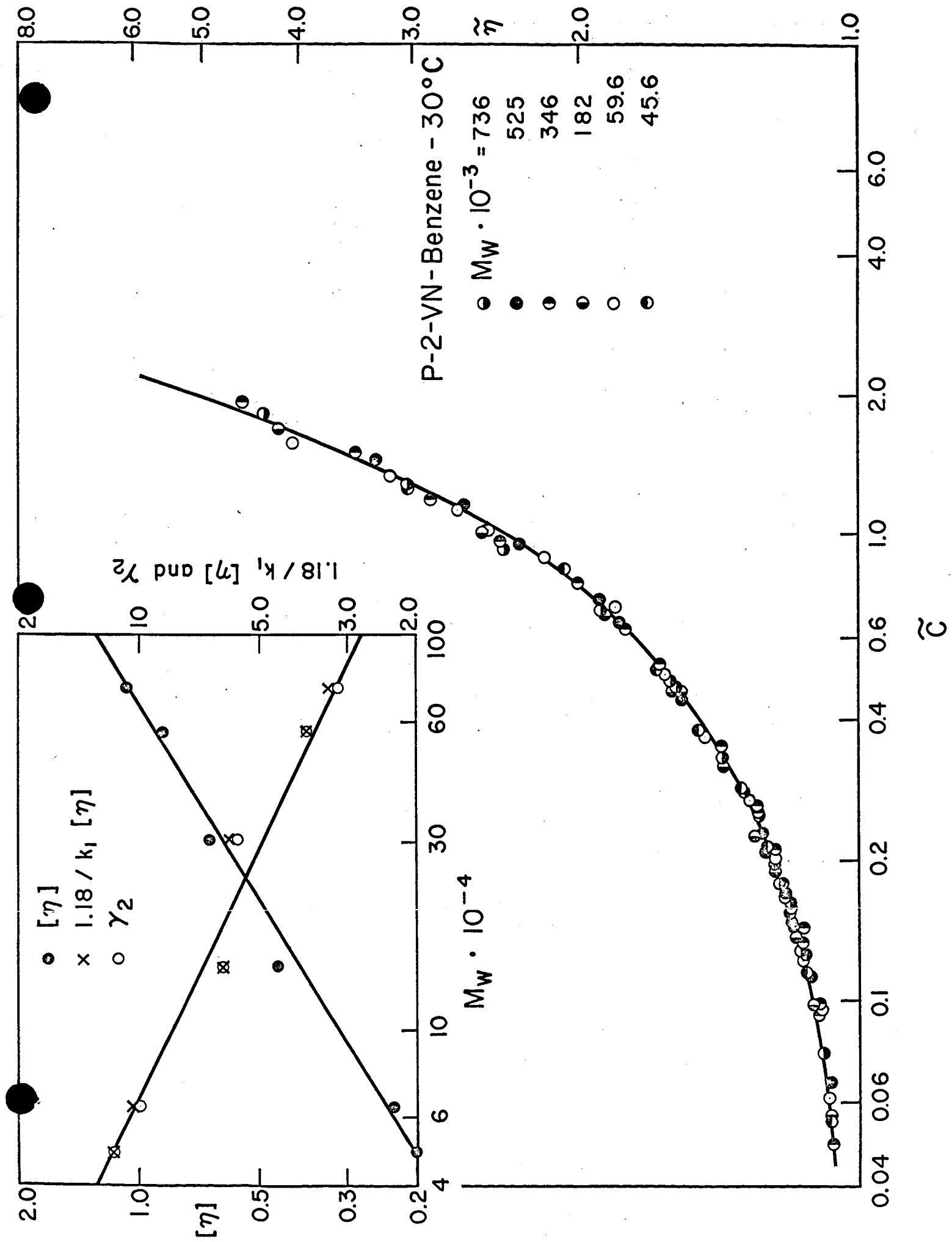
TABLE V

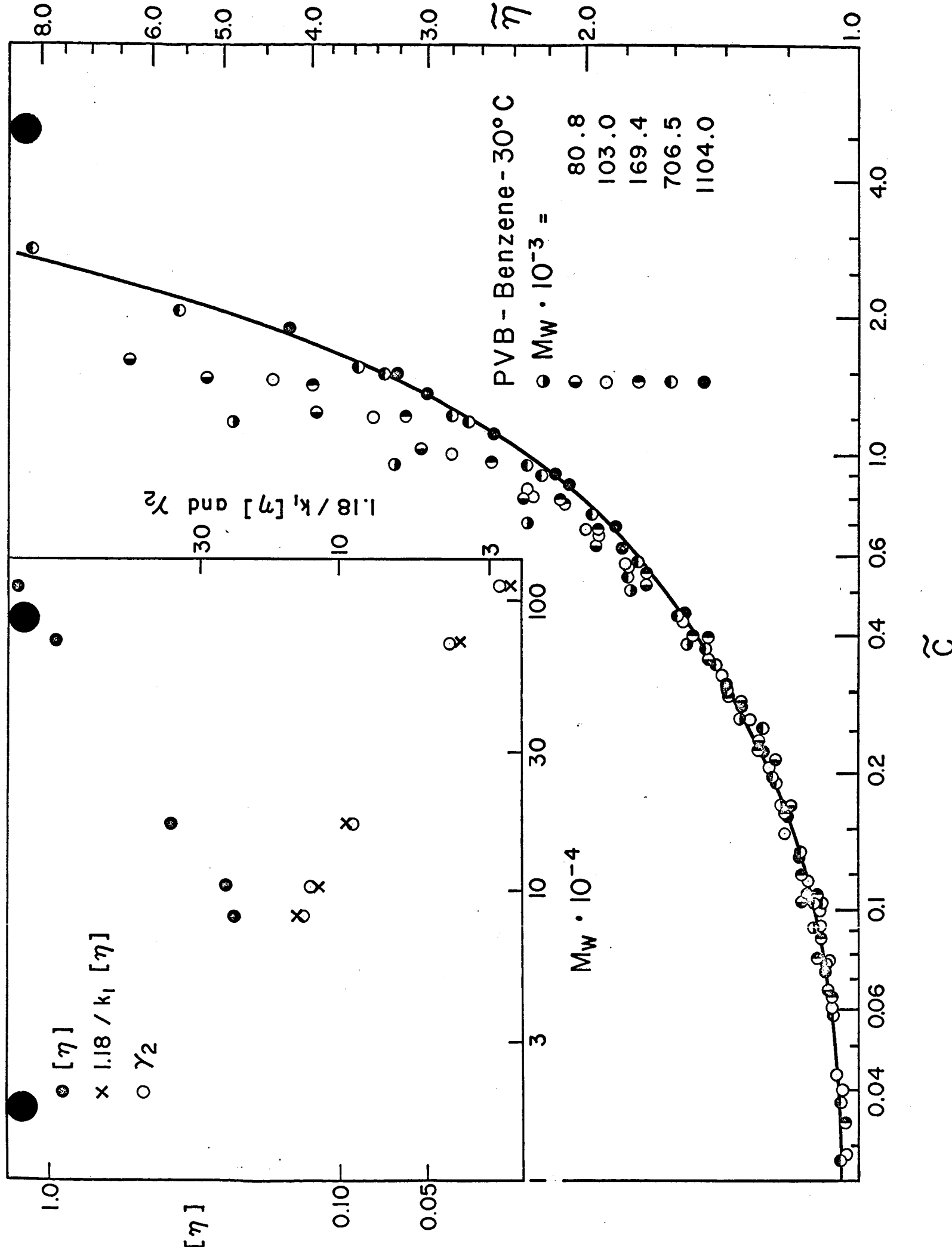
Molecular weight dependence parameters of $[\eta]$ and γ and interaction constants for some vinyl polymers.

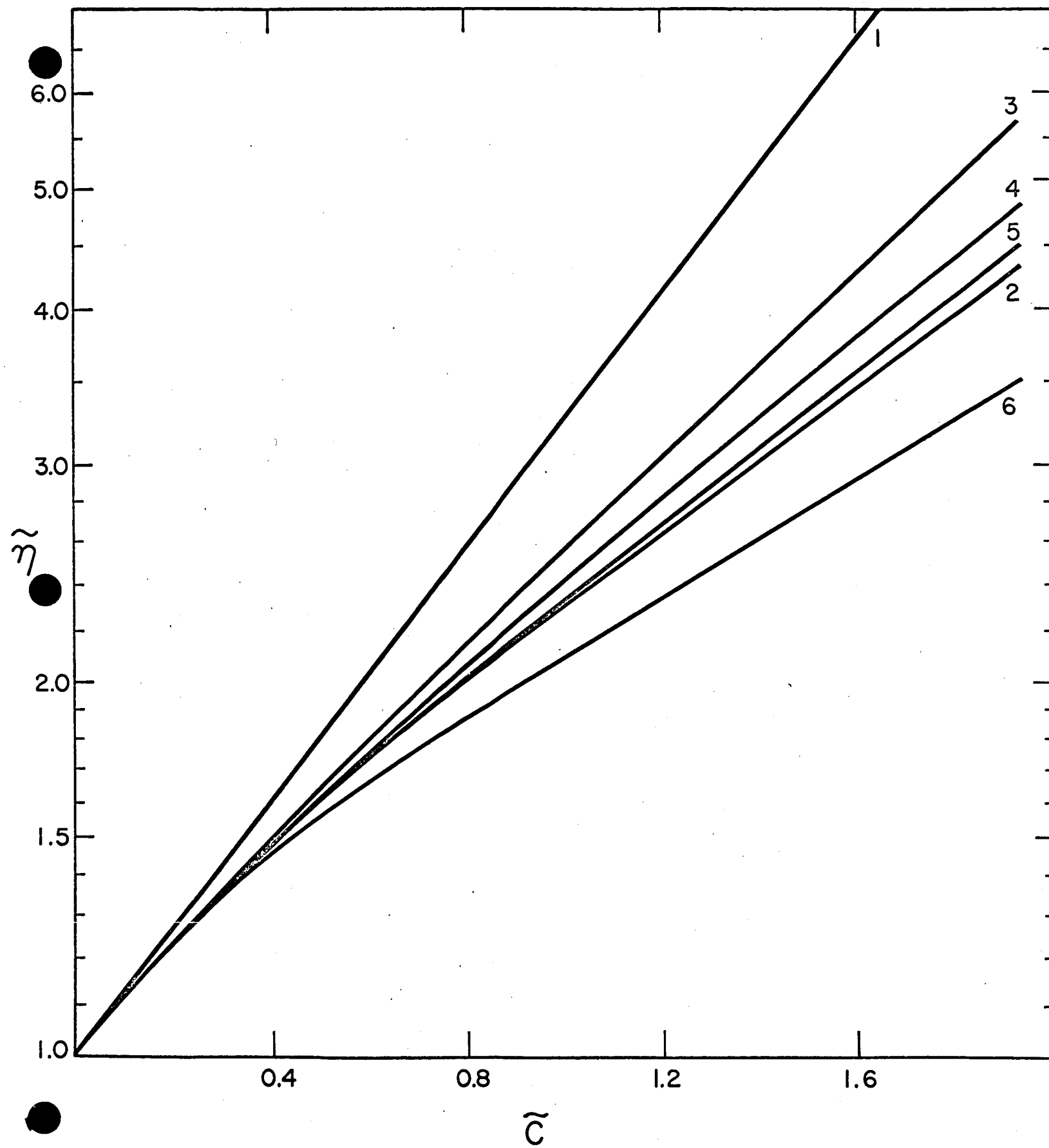
No.	Polymer	Solvent	Temp. (°C)	$K \cdot 10^4$	a	$K_L \cdot 10^{-4}$	a_L	$M^*_O L_L \cdot 10^{-2}$	Λ	A_O (Å)	$B \cdot 10^{27}$ (ml)	Ref.	
1	PS	Cyclo- hexane	34.4	9.02	0.503	0.1382	0.471	52	2.149	1.0	4.83	0	8
2	PS	Toluene	30	0.92	0.72	1.11	0.64	52	8.853	4.1196	4.83	2.4	1
3	P-1-VN	Benzene	30	0.198	0.826	1.356	0.628	77	8.861	4.1233	3.99	2.6	this work
	"	"	25	2.55	1.85	-----	-----	77	-----	-----	-----	---	9
	"	"	25			-----	-----	77	-----	-----	-----	---	4
4	P-2-VN	Benzene	30	2.69	0.615	0.216	0.482	77	2.662	1.2387	5.84	0.69	this work
	"	"	17	0.17	0.8	-----	-----	77	-----	-----	-----	---	10
	"	"	20	0.66	0.71	-----	-----	77	-----	-----	-----	---	11
	"	"	25	0.95	0.70	-----	-----	77	-----	-----	-----	---	4
5	PVB	Benzene	30	1.174	0.666	1.366	0.609	90	8.816	4.1024	4.56	2.5	this work
	"	"	25	0.192	0.69	-----	-----	90	-----	-----	-----	---	12,4
6	PVC	Cyclo- hexanone	30	0.60(1.63)	0.86(0.77)	0.3473	0.65	31.3	3.703	1.723	4.10	0.93	16a(b)

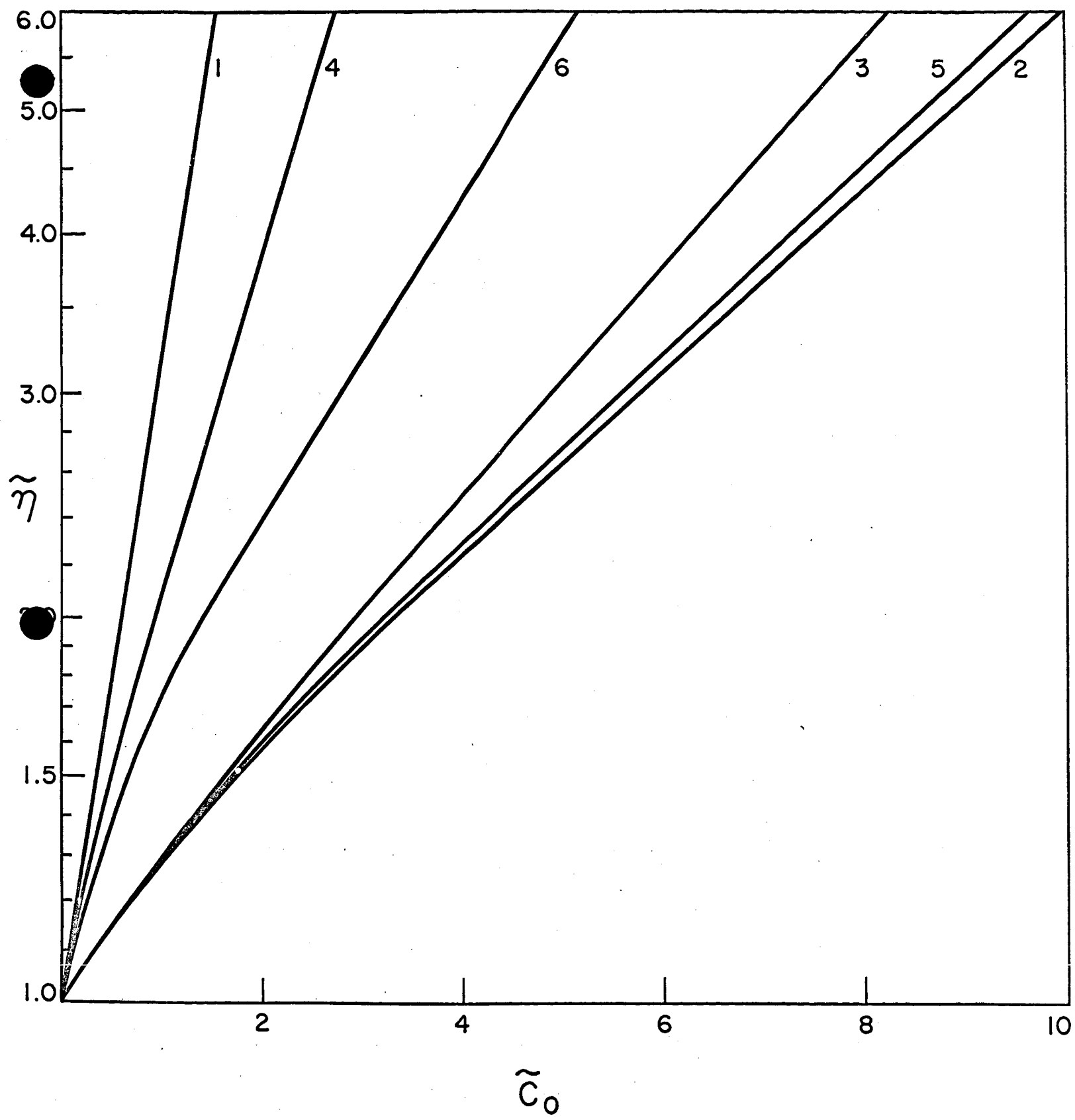
* M_o is a molecular weight calculated per carbon atom of polymer backbone chain.











CORRESPONDING STATE RELATIONS FOR THE NEWTONIAN
VISCOSITY OF POLYMER SOLUTIONS.

II. FURTHER SYSTEMS AND CONCENTRATED SOLUTIONS.*

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SYNOPSIS

In earlier work we have indicated a superposition principle for moderately concentrated mixtures ($c \lesssim 2/[\eta]$, in g/dl) in good and poor solvents. By an examination of data on a number of vinyl polymers and cellulose derivatives in good as well as poor solvents, the validity of this principle is extended to concentrated solutions ($c \lesssim 50\%$). The characteristic concentration factor^{1,2} γ is proportional to M^{-a_1} over the whole concentration range, with $0.47 \leq a_1 \leq 1.10$ being larger for good than for poor solvents, the result obtained earlier. Significant deviations from this relationship are noted in good solvents for those low molecular weights, which also deviate from the usual intrinsic viscosity relationship. This may be related to the expansion factor of the polymer coil.

Based on these results, the concentration and molecular weight dependence of the viscosity in the concentrated solution can be related to each other in terms of the parameter a_1 , and thus to thermodynamic

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characteristics. In this manner a bridge between the relatively dilute and concentrated regions is established. Currently used semiempirical expressions are analyzed in terms of these results. For the polystyrene - cyclohexane system and $\theta - 9 \leq T \leq \theta + 3$, γ can be identified with the critical concentration for phase separation. Provided an "entanglement" concentration c_e exists, in the neighborhood of which the concentration dependence of the viscosity changes rapidly, γ can alternatively be shown to be proportional to c_e , or $c_e \propto M^{-a_1}$. The temperature reduction scheme suggested earlier remains to be investigated.

I. INTRODUCTION

In previous papers^{1,2} we have developed a procedure for the description of viscosity-concentration functions which leads to master curves over a wide range of molecular weights. Moreover it was possible to relate in poor solvents (T in the neighborhood of θ) the characteristic concentration γ to a thermodynamic parameter, namely the critical concentration for phase separation. The polymers studied in one or several solvents were polystyrene, polymethyl methacrylate and a copolymer of these. As a corollary of these results the Huggins parameter k_1 becomes a slowly varying inverse function of M . More recently³ it was shown that the concentration c_1 , at which conventional plots of η_{sp}/c exhibit an upswing, usually ascribed to adsorption effects, is proportional to γ .

The results so far presented apply to relatively low concentrations of the order of $2/[\eta]$. The purpose of this paper is twofold. First, we wish to extend our considerations to further polymer-solvent systems, both good and poor, which have become available in a similar range of

concentrations. Secondly we shall investigate by means of chemically very different polymers, to what extent our previous considerations may be generalized to include the concentrated range, which encompasses the so-called entanglement region.

II. MODERATE CONCENTRATIONS

1. Polystyrene: Previous measurements^{1,2} on the polystyrene - cyclohexane system in the neighborhood of the θ - temperature, $t = \theta + \delta$, $\theta = 34.4^\circ\text{C}$, have been extended⁴ to $\delta = +3, -6$, and -9 . Fig. 1 exhibits the functions

$$\eta_{sp}/(c[\eta]) \equiv \tilde{\eta} = \tilde{\eta}(\tilde{c}); \quad \tilde{c} \equiv c/\gamma \quad (1)$$

The γ 's used for the seven anionic polymers are those previously determined¹ with $M_n = 1.46 \times 10^5$ selected as the reference sample for toluene. For cyclohexane, $\gamma \equiv c_{cr}$, the critical concentration for phase separation. A good fit is noted over the whole range of temperatures. Moreover, there appears a definite straight line portion, i.e., the Martin relation is here obeyed. In the same plot, the results for toluene¹ at 30 and 48°C are recapitulated for comparison. Finally there appears the function; $\eta_{sp}/2.5\phi$ (where ϕ is a volume fraction of a suspension), derived by Simha and Somcynsky for spherical suspensions.⁵ The reducing concentration ϕ_{max} here corresponds to close packing. The approach to this function by polymer solutions, as we pass from good to poor solvents, is noted.

2. Polyisobutene: Recently, Lung-Yu Chou⁶ investigated a good (cyclohexane, 25°C) and a θ - solvent (benzene, 24°C) up to viscosities of 14 centipoise. The four fractions range in M_v from 1.05×10^4 to 1.08×10^6 . Fig. 2 shows the results, and the similarity with Fig. 1

is noted. Fig. 3 depicts the molecular weight dependence of γ and the product $k_1[\eta]$, which is given by:

$$\gamma \propto 1/(k_1[\eta]) \quad (2)$$

$$\text{with } \gamma = \text{const. } M^{-a_1} \quad (3)$$

and $[\eta] = \text{const.} \cdot M^a$. The reference sample has a molecular weight $M_v = 5.9 \times 10^4$. From Fig. 3 we obtain: for the θ - solvent, $a_1 = 0.47$, for cyclohexane, $a_1 = 0.64$. In the construction of these lines the independent γ and $k_1[\eta]$ -data were used simultaneously. This result may be compared with $a_1 = 0.47$ and 0.64 for polystyrene in θ and toluene respectively. Considering procedural and experimental sources of error in determining γ and $k_1[\eta]$, the fit in Fig. 3 is quite adequate. However, in benzene the deviation of the highest molecular weight from the master curve, Fig. 2, is significant, but the experimental data themselves do not follow a smooth relation.

III. ELEVATED CONCENTRATIONS

1. Poly(vinyl chloride): Pezzin and Gligo⁷ have presented viscosity data for eight fractions and two blends in cyclohexanone. The weight average molecular weights ranged from about 10^4 to 2.3×10^5 , the concentrations from approximately 0.2 to 41 wt. % and the viscosities from 0.02 to 133 poise. In Fig. 4, the logarithmic dependence of η on c is presented. Here the reference molecular weight is 1.1×10^5 . A satisfactory superposition is achieved for both fractions and blends with the exception of the lowest fractions ($M_v = 10,500$ and $26,000$) which produce significant deviations. These are also noted in the plot of γ . The line pertaining to the product $k_1[\eta]$ has been drawn with the

same slope. It is suggestive, but not conclusive, that polydispersity is a factor in this quantity. This would be in accord with similar observations on polystyrene in toluene¹ ($k_1[\eta]$ vs. M_n plotted). The magnitude of $a_1 = 0.65$ is about what one would expect for a good solvent, $a = 0.84$ at 25°C,⁷ although the magnitude of the exponent a seems surprisingly high.

2. Polyisobutene: Data for four samples in xylene and three samples in decalin at 25°C, both fairly good solvents, were obtained by Johnson et al.⁸ The molecular weights M_v range from 3.2 to 40×10^5 , the concentrations from 0.6 to 40 wt. % and the viscosities from 0.15 poise to 268 kilopoise. The reduced plots appear in Fig. 5 with $\gamma = 1$ for $M_v = 3.2 \times 10^5$, and very good superposition can be accomplished in both solvents. The arrows mark the "critical" entanglement concentration for the particular molecular weight indicated. The \tilde{c}_e 's were computed from the relation³⁹ $c_e = 3.92 \times 10^6/M$ and the known γ . Once more the numerical value of the coefficient a_1 is characteristic of a good solvent.

We have treated additionally in Fig. 6 data for polyisobutene in isooctane.⁹ Here the molecular weights (M_v) extend from 900 to 2.5×10^6 and the concentrations from 0.5 vol. % to the melt. The transformation of the data into our system of coordinates is made difficult without the use of the experimental numerical values, rather than graphs, and by the absence of information about the $[\eta]$'s. Thus, a double shift on the logarithmic scale is required. All this results in a considerable scatter in Fig. 6, based on $\gamma = 1$ for 6.4×10^5 . It is presented here to illustrate once more the departures for the lowest molecular weights, that is, $M_v = 900$ and 2×10^4 . Smaller deviations may also be noted for

$M_v = 1.1 \times 10^5$ at more elevated concentrations. The \tilde{c}_e 's were computed from the viscosity - molecular weight relations for different concentrations.⁹

3. Polyvinyl alcohol: Aqueous solutions of 27 samples with $2.4 \times 10^4 \leq M_w \leq 32 \times 10^4$ were analyzed¹⁰ at 30°C with the concentrations varying from 4 to 20 g/dl and the viscosities from 2 centipoise to 210 poise. Fig. 7 exhibits a very good superposition with $\gamma = 1$ for $M_w = 6.12 \times 10^4$. The range of entanglement "points" is indicated. The value for a_1 is one of the highest yet observed for vinyl polymers.

4. Cellulose derivatives: We examine ethyl cellulose¹¹ in a toluene-ethanol mixture (4:1) at 25°C and cellulose acetate¹² in acetone at 20°C. The usual plots are shown in Fig. 8. The intrinsic viscosities lie between 0.5 and 2.2 in the former and 0.47 and 2.58 in the latter, with the solution viscosities increasing to 49 and 51 centipoise. We estimate from the results given¹² that M_w extends from 1.7 to 9.0×10^5 for both polymers, based on Staudinger's rule. Correspondingly, the coefficients a_1 are comparatively high, but once more higher in the better solvent.

5. Polyisoprene: Recently Fetters¹³ published viscosity data on 22 polymer fractions ($M_w/M_n = 1.03 - 1.11$) over a wide range of molecular weights ($2.5 \times 10^4 \leq M_v \leq 1.3 \times 10^6$) in decane at 25°C. However, only three concentrations at most were examined. Thus we can not establish the $\tilde{\eta} - \tilde{c}$ function, but exhibit instead in Fig. 9 plots of $\log(\text{const. } \eta)$ vs. $\log M_v$. Clearly it should be possible to derive a single function from these results. From the vertical and horizontal shifts of "critical" entanglement points we estimate $a \approx 0.86$ and

$a_1 = 1.08$, surprisingly large values. However, in toluene at 25°C, $a = 0.82$ has been cited.¹³

IV. DISCUSSION

The polymer-solvent systems analyzed and their smoothed master curves are summarized in Table I and Fig. 10. From the results discussed we conclude that eq. (1), as a molecular weight independent relation, is obeyed over the whole range of concentrations available, rather than the restricted range studied earlier.^{1,2} One exception is to be noted, i.e., good solvents and low molecular weights, as seen in polyisobutene - isooctane⁹ ($M \leq 2 \times 10^4$); poly(vinyl chloride) - cyclohexanone⁷ ($M \leq 2.6 \times 10^4$); polystyrene - toluene² ($M \leq 1.5 \times 10^4$); also poly(ethylene glycols) of low molecular weight in five different solvents.¹⁴ We recall that this is about the range in which the exponential $[\eta] - M$ relation breaks down.^{15, 16} However, this latter observation applies to poor solvents as well.

In eq. (1) the concentration factor γ is characteristic of the polymer-solvent system^{1, 2} and depends on molecular weight according to eq. (3). In the polystyrene solutions investigated it was not necessary to allow for a variation of γ over our temperature range in either good or poor solvents. It is, of course, possible to derive explicit analytical expressions from Fig. 10. They would not be of simple form over the whole range of reduced concentrations and therefore we have not developed them. There exist currently empirical and semi-empirical expressions for the viscosities of polymer melts and concentrated solutions as a function of concentration and molecular weight,

some of these based on the concept of a "critical" entanglement molecular weight M_e and on a formal analogy between dilute and concentrated solution viscosities. In what follows these are compared with the consequences of eq. (1).

Consider first the approximate representation:⁸

$$\eta = \text{const. } c^{\epsilon_1} \times M^{\epsilon_2} \quad (4)$$

where the ϵ_i are taken to be numerical factors. Table II lists several examples for eq. (4) in the intermediate range of concentrations, $c \leq 40\%$, and also systems where one or both coefficients vary with c and/or M . In general, the changes in ϵ_2 are smaller than those in ϵ_1 , but nonetheless significant. Even in the melt, ϵ_2 does not seem to assume a universal value, (see also below). The discussion proceeds most conveniently through the derivatives of eq. (1), viz.:

$$v_1 = (\partial \ln \tilde{\eta} / \partial \ln c)_M; \quad v_2 = (\partial \ln \tilde{\eta} / \partial \ln M)_c$$

The corresponding unreduced derivatives are then ϵ_1 and ϵ_2 . From eqs. (1), (3) and (4) there follows:

$$v_1 = \eta_r \epsilon_1 / (\eta_r - 1) - 1; \quad v_2 = (v_1 + 1)(\epsilon_2 / \epsilon_1) - (a_1 v_1 + a) \quad (5)$$

where $\eta_r = \eta_{sp} + 1$.

But if our superposition principle, eq. (1) is to hold, then $v_2 = 0$ and

$$a_1 \epsilon_1 = \epsilon_2 + (a_1 - a)(1 - 1/\eta_r) \quad (5a)$$

Provided $\eta_r \gg 1$, then eq. (5a) is either consistent with constant ϵ_1 and ϵ_2 or predicts a definite correlation between the variations of ϵ_1 and ϵ_2 , which is independent of concentration or molecular weight, as long as a_1 and a may be regarded as constants. It will have been

noted that the differences $a_1 - a$ are small. A more detailed analysis of low concentration data shows³³ that $|a_1 - a| \leq 0.2$. Accepting therefore values for ϵ_2 of the order of 3 - 4 or larger above the "critical" chainlength Z_e , (5a) simplifies further to $a_1 \epsilon_1 = \epsilon_2$. Since both a and a_1 reflect thermodynamic effects, being lower in poor than in good solvents,^{1, 2} we must conclude that at least in the intermediate range of concentrations, $c \leq 50\%$, thermodynamic effects continue to determine the concentration dependence of the viscosity, as they do at lower concentrations. This is true even if ϵ_2 is constant and thus both above and below M_e . An increase of ϵ_1 from good to poor solvent is expected, but eqs. (5) and (5a) present a definite correlation between the low and the intermediate concentration range.

If ϵ_1 is constant, then $\tilde{\eta} \propto \tilde{c}^{\epsilon_1 - 1}$ in accord with the straight line portions in Fig. 10. In Table III the experimental and computed (eq. (5a)) ϵ_2 are shown. In the c -range considered, $50 \leq \tilde{\eta} \leq 1000$. In this interval the curvature of the $\tilde{\eta} - \tilde{c}$ function is small and the v_1 - values quoted in Table III represent difference quotients. The agreement is very gratifying indeed, in view of the fact that the ϵ_i are determined from one set of curves, a_1 from our superposition procedure and a at infinite dilution. These results support once more the validity of the corresponding states principle, $v_2 = 0$.

In recent years, Allen, Berry and Fox^{34,35,36,37} have reconsidered the concentration and molecular weight dependence of the viscosity. Taking the polymer melt as their starting point, they develop an expression for a "corrected" η_{corr} , which contains a first and 3.4 power dependence on M below and above the "entanglement" chainlength

Z_e of the melt respectively. To compare these results with ours, we resort to the logarithmic derivatives ϵ_i^* , defined in terms of η_{corr} . However, the equations of Fox and Allen contain the glass transition temperature T_g and further parameters. A general analysis would require an adequate knowledge of these as a function of c and M . The M - dependence is more readily evaluated and accepting a familiar dependence of T_g on the number of chain ends, we obtain:

$$\epsilon_2 = \epsilon_2^* + KkT_g^2 / [(T - T_0)^2 \eta_n]$$

$$\text{with } \epsilon_2^* = 1, \quad Z_n \leq Z_e; \quad \epsilon_2^* = 3.4, \quad Z_n \geq Z_e \quad (6)$$

$$\text{and } T_g^{-1} = [T_g(\infty)]^{-1} + k/Z_n + k_1(1-\phi)$$

K and T_0 are functions of the volume fraction ϕ of polymer, and k and k_1 are characteristic of the specific polymer and polymer-solvent system respectively.³⁶ Equation (6) predicts an increase of ϵ_2 with decreasing Z_n , if T_0 is assumed to be constant and considering the weak dependence³⁸ of T_g on Z_n . The numerical effect may be minor but it is worth noting that for polyvinyl alcohol-water mixtures, Oyanagi and Matsumoto¹⁰ observe $\epsilon_2 \approx 4.3$ for $Z > 2.5Z_e$, whereas $\epsilon_2 = 3.4$ for $Z_e < Z < 2.5Z_e$. A qualitatively similar behavior is observed for polyisobutene in isooctane,⁹ and in some other systems as well.³⁹ According to the correction term given,³⁵ $\epsilon_2 \geq \epsilon_2^*$, and ϵ_2 should decrease to 3.4 for increasing $Z > Z_e$. Experiments indicate opposite behavior.

We can be more specific by considering poly(vinyl acetate) mixtures in cetyl alcohol and diethyl phthalate.²⁸ The equation proposed for both solvents with a stated accuracy of $\pm 10\%$ in η , for $0.09 \leq \phi \leq 1$ and over a wide range of temperatures, leads to the following results:

$$\begin{aligned} \epsilon_1 &= 3.71 + 6.1 \times 10^{10} \phi e^{1.95\phi/T^4}, \quad \epsilon_2 = 3.4; & \text{for } Z > Z_e \\ \left. \begin{aligned} \epsilon_1 &= \epsilon_1(Z > Z_e) + 0.6(1 - 0.6\phi)^{-2} \phi \ln(Z\phi/690) + \epsilon_2 - 3.4 \\ \epsilon_2 &= (1 - 0.6\phi)^{-1}; \end{aligned} \right\} & \text{for } Z \leq Z_e \end{aligned} \quad (7)$$

Now eq. (5a) remains valid for non-constant ϵ_1 and the predicted concentration dependence of ϵ_1 according to eq. (7) is pronounced. For example, at $T = \theta = 123^\circ\text{C}$ for cetyl alcohol, $\epsilon_1(Z > Z_e)$ increases from 4.01 to 7.0, as ϕ varies from 0.1 to 0.5, the range of interest here. Since $\eta_r \gg 1$, this is inconsistent with eq. (5a) for constant ϵ_2 , which would demand a change in a_1 from 0.96 to 0.48, with $a = 0.50$. For $Z = Z_e/2$, ϵ_2 varies from 1.06 to 1.43 and ϵ_1 from 2.52 to 4.60 over the same range. These results demand a change of the apparent a_1 from 0.26 to 0.34. Of course, a scatter of $\pm 10\%$ will be excessively magnified in the derivatives and a decisive comparison necessitates a superposition test of the actual experimental data. The differences between ϵ_1^* and ϵ_1 become insignificant for sufficiently large molecular weights. In eq. (7) the chain length does not appear for $Z > Z_e$ and our conclusions are not affected by the Fox-Allen corrections.³⁵

From ϵ_1 , eq. (7), one can obtain $v_1 = \epsilon_1 - 1$ in the θ - solvent. Up to $\phi \approx 0.4$, v_1 is nearly linear in ϕ and independent of Z for $Z < Z_e$, increasing rapidly thereafter. For $Z > Z_e$ this linearity holds over a more restricted range of ϕ . This is consistent with the validity of the Martin relation (the straight lines in the reduced plots of Figs. 1 and 2), observed for other θ - systems and lower concentrations.

From the superposition principle we obtain as a corollary a relation for the molecular weight dependence of the "entanglement concentration" ϕ_e or c_e and the corresponding viscosity η_e . This concentration is defined by the general conditions

$$\eta = \eta(c, M), \quad c \geq c_e; \quad \eta^{(1)} = \eta^{(1)}(c, M), \quad c \leq c_e;$$

$$\eta = \eta^{(1)}; \quad c = c_e$$

where η and $\eta^{(1)}$ represent two different functions. From these relations, the definitions of the ϵ_i , now taken above and below M_e , and eq. (5a), we observe that

$$(\text{d} \ln c / \text{d} \ln M)_{c=c_e} = (\epsilon_2^{(1)} - \epsilon_2) / (\epsilon_1 - \epsilon_1^{(1)}) = -a_1$$

$$\text{or } c_e(M) = (M_e/M)^{a_1}; \quad (\eta_r - 1)_e \equiv [\eta] \gamma \tilde{c}_e \tilde{\eta}(\tilde{c}_e) \propto M^{a-a_1}; \quad (8)$$

where $c_e = 1$ for $M = M_e$, the "critical" molecular weight for the melt. In other words, $\tilde{c}_e = \text{const.}$ for a given polymer independently of the solvent, provided the same reference molecular weight M_r is used in the $\gamma - M$ relation, viz. $\gamma = (M/M_r)^{-a_1}$. It follows from eq. (8) that $c_e(M)$ is smaller in the better solvent. One may speculate that the more compact average conformation in the poorer solvent makes the kind of entanglements pictured in current interpretations more difficult to accomplish. It should be noted that a proportionality of c_e with the inverse first power^{13,20,29,34} as well as the^{inverse} square root^{19,20} has been advocated, which may be regarded as special cases of our result. Of course, for volume fractions close to unity, it is difficult to discriminate experimentally between one or the other power. In our opinion the spread of the \tilde{c}_e - values of Figs. 5 and 6

results from the adoption of the first instead of a fractional power in eq. (8).

Next we refer to the results of Busse and Longworth.²³ These authors average the molecular weight over the solute and solvent (or low molecular weight additive) and write in terms of weight fractions w_i .

$$\eta = \text{const. } \bar{M}_v^{3.4}$$

$$\text{with } \bar{M}_v^{a^*} = w_1 M_1^{a^*} + w_2 M_2^{a^*}$$

Now for sufficiently large w_2 and small M_1 ,

$$(\partial \ln \eta / \partial \ln w_2)_M = 3.4/a^*$$

The authors observe that $a^* = a \pm 0.2$ for a series of hydrocarbon and polyethylene mixtures. Since the derivative represents ϵ_1 , eq. (5a) simplifies here to $a^* = a_1$. This result holds for any constant value of ϵ_2 .

The reduced plots encompass both mixtures and pure polymers. When solutions and a melt occupy the same region of the $\tilde{\eta} - \tilde{c}$ plane, it implies that the molecules are in the same hydrodynamic and thermodynamic environment. In comparing, for example, a melt with a solution of a higher molecular weight, the solvent leads to a reduced effective average molecular weight. This general idea, of course, has been expressed earlier, but it is made more precise by means of our reduced functions and related to the behavior in dilute solution. Simple relations for the molecular weight dependence are readily obtained. Consider a particular polymer series in a given solvent. A parti-

cular value of $\tilde{\eta} = \text{const.}$ may represent a solution: $\tilde{\eta} = \tilde{\eta}(c, M)$ and a melt: $\tilde{\eta}_m = \tilde{\eta}_m(M_m)$. Provided the intrinsic viscosities obey the identical exponential relationship, and since $\tilde{\eta} = \tilde{\eta}_m$ the logarithmic derivatives in respect to molecular weight are equal or $\epsilon_2 = \epsilon_{2m}$, and $\epsilon_2(\tilde{\eta}_1) \neq \epsilon_2(\tilde{\eta}_2)$ if $\tilde{\eta}_1 \neq \tilde{\eta}_2$.

Finally it is interesting to speculate on the origin of the differences between θ and good solvents where our superposition scheme breaks down at sufficiently low molecular weights, see p. 7. By analogy with the deviation for the intrinsic viscosity, we would expect deviations at $T = \theta$ as well, but at still lower chain lengths. We tentatively propose the following interpretation. For moderately concentrated solutions, one of us has suggested an equation for the change of the expansion factor α with \tilde{c} , viz.:⁴⁰

$$\alpha(\tilde{c}, z) = \alpha_0(z) / [1 + \tilde{c}F(z)]$$

where z is the usual thermodynamic parameter, $F(z)$ is a weak function of z , with $F(\theta) \approx 0$, and α_0 refers to infinite dilution. If one assumes that also at finite concentrations the viscosity can be related to an effective hydrodynamic volume, then it is pertinent to consider the derivative

$$(\partial \ln \alpha / \partial M)_{\tilde{c}, T} = A(1 - 2x) / [6\alpha_0^3 M^{1/2}(1 - x)]$$

where $x = [a - 3/(3\alpha^2 + 1)]\tilde{c}F/(1 + \tilde{c}F)$ and $A = 2.053z/M^{1/2}$. At low concentrations x is small and the derivative will vary essentially as $M^{-1/2}$. As \tilde{c} and x increase, the derivative decreases for all molecular weights, although the actual relations used were developed for $\tilde{c} \leq 1$ only. Thus at low concentrations the deviations for small M should

be more pronounced than at elevated concentrations. However, our fitting procedure, based on horizontal shifts in the $\log \tilde{\eta} - \log c$ plane, gives more weight to the low concentrations and this is reflected in deviations in the upper range.

These considerations would furthermore suggest that in order to achieve superposition for all molecular weights, experimental data be compared at corresponding temperatures, defined in terms of z . Equivalently, the ratio $z/z_{cr} = T_{cr}(T - \Theta)/[T(T_{cr} - \Theta)]$ may be chosen, as was suggested earlier.² Here the subscript refers to the thermodynamic critical condition for mixing.

In Fig. 1 we have noted the steady increase in the slopes of the semilogarithmic reduced viscosity-concentration functions, as the solvent changes from good to Θ and $T < \Theta$, and the approach to the curve representing hard sphere suspensions. It would be of interest to investigate solutions near their respective critical temperatures, $z/z_{cr} = 1$. A universal curve, independent of molecular weight should result and be compared with the hard sphere result.

Such investigations should indicate the comparative role of ϕ_{max} and the characteristic concentration factor γ . What we know so far is that near $T = \Theta$, γ^{-1} can be identified with $c_{cr}^{-1} \propto [\eta](T = T_{cr})$, the intrinsic viscosity, or approximately the encompassed coil volume at the critical temperature.² This result will not necessarily hold for all temperatures below Θ . As we have shown on the other hand in eq. (8), γ can alternatively be related to a characteristic quantity in concentrated solution, that is, the "entanglement" concentration c_e , at which the molecular weight depen-

dence of the viscosity changes rapidly, and the characteristic molecular weight M_e of the melt. The result is

$$\gamma = (M_r/M_e)^{a_1} \cdot c_e \quad (8a)$$

This equation can, of course, hold only for sufficiently large molecular weights. It should be noted that the entanglement molecular weights reported are larger than the lower limits of applicability of our superposition scheme in solution. These limits appear to be close to the M_e - values for melts reported in the literature.

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TABLE I

Characteristics of Polymer-Solvent Systems

No.	Polymer	Solvent	Temp. °C	Mol.Weight $M_v \cdot 10^{-4}$	Concentration Range	η_{\max} poise	No. of Samples	a	a_1	Ref.
1	Polystyrene	Cyclohexane	34.4=0	1.5-60*	0-22 g/dl	0.17	9	.503	.47	1
2	Polystyrene	Toluene	30	1.5-60*	0-9 g/dl	0.5	9	.72	.64	1, 19
3	Polyisobutene	Benzene	24=0	$1.0 \cdot 10^2$	0-7 g/dl	0.14	4	.50	.47	6
4	Polyisobutene	Cyclohexane	25	$1.0 \cdot 10^2$	0-5 g/dl	0.18	4	.72	.64	6
5	Polyisobutene	Xylene	25	32-400	5-40 wt%	210	5	.64	.68	8
6	Polyisobutene	Decalin	25	100-251	12-25 wt%	$2.7 \cdot 10^5$	3	.65	.68	8
7	Polyisobutene	Isooctane	20	0.09-250	5-100 vol%	10^{11}	7	.58(?)	.65	9
8	Poly(vinyl chloride)	Cyclohexanone	30	1.05-23	0-41 wt%	133	10	.86	.65	7
9	Polyvinyl alcohol	Water	30	2.44-32.2	4-20 g/dl	$2 \cdot 10^4$	27	.64	.69	10, 19, 25
10	Ethyl cellulose	Toluene:Ethanol 4:1	25	12-90	0.8-13 vol%	50	4	.1.0	.73	11
11	Cellulose acetate	Acetone	20	17-90	0-4 vol%	0.35	6	.1.0	.88	12
12	Polyisoprene	Decane	25	2.52-126	4.9-19.2 wt%	12	22	.86	1.08	13

*Number average molecular weights.

TABLE II

Numerical values of exponents ϵ_1 and ϵ_2 , eq. (4).

No.	System Polymer - solvent, °C	ϵ_1		ϵ_2		Ref.
		$Z < Z_e$	$Z > Z_e$	$Z < Z_e$	$Z > Z_e$	
1	Polystyrene - diethylbenzene	2.4	6 - 25	1.0	3.4-4.5	17
2	Polystyrene, 217	---	---	1.3	3.7	18
3	Polystyrene - toluene	2.3	5.0	---	3.4	19
4	Polyethylene, 190	---	---	1.7*	3.4	20,21
5	Polyethylene, 150	---	---	---	3.4-5.8	22
6	Polyethylene - wax	---	3.4/a=4.5-12**	---	3.45	23
7	Polyisobutene - xylene	---	5.0	---	3.4	8
8	Polyisobutene - decalin	---	5.0	---	3.4	8
9	Polyisobutene - isooctane	0.9-5.0	5.0-19.0	0.25-1.1	3.4	9†
10	Polyisobutene, 217	---	---	1.4	3.6	24
11	Polyvinyl alcohol - H ₂ O	5.0	6.0	1.0	3.4-4.3	25
12	Polyvinyl alcohol - H ₂ O	4.4	6.0	---	3.4	19
13	Polyvinyl alcohol - H ₂ O	2.0	4.3	0.7	3.3	10
14	Poly(methyl acrylate) - diethyl phtalate	3.1	5.0	---	---	26
15	Cellulose trinitrate - isophorone, 35	3.0	5.0-20	---	---	27
16	Polyisoprene - decane, 25	1.5	3.25	1.0	3.2	13
17	Polyvinyl acetate - diethyl phtalate, 50-157	eq.(7)	eq.(7)	eq.(7)	3.4	28
18	Polyvinyl acetate - cetyl alcohol, 123-157 [A(T) = 6.106 × 10 ¹⁰ × T ⁻⁴]	eq.(7)	eq.(7)	eq.(7)	3.4	28
19	Polyvinyl chloride - cyclohexanone, 30	0.18	4.74	0.23-1.07	1.88- 4.05	7†
20	Cellulose acetate - acetone, 20	0.16	3.6	0.55	4.1	12†
21	Poly(methyl methacrylate) - diethyl phtalate, 120	3.0	42	1.4	3.4	29
22	Poly(methyl methacrylate) - diethyl phtalate, 60	3.0	80	1.4	3.4	29
23	Polydimethyl siloxane, 25	---	---	1.3	3.5	30
24	Polydimethyl siloxane, 25	---	---	1.4	>4.1	31
25	Polysilicones, 25	---	---	1.39	3.7	32

† ϵ_1 calculated by us; * n-alkanes(ref. 29); ** a from $[\eta] \propto M^a$.

TABLE III

Application of Eqs. (5) and (5a) to some Systems of Table I.

No. of system in Table I	v_1 $50 < \tilde{\eta} < 1000$	a_1 from γ 's	a	ϵ_2 , exp. $50 < \tilde{\eta} < 1000$	ϵ_2 , eq. (5a)
5	4.2	0.68	0.64	3.4	3.5
6	4.1	0.68	0.65	3.4	3.4
7	4.3	0.65	0.58(?)	3.4	3.4
8	4.1	0.65	0.86(0.77)*	3.4	3.6(3.4)*
9	3.8	0.69	0.64	3.4	3.3

* Larger value from ref. 7, smaller from ref. 41.

LEGENDS FOR FIGURES

Fig. 1. Curve A, reduced viscosity quantity $\eta_{sp}/(2.5\phi)$ as a function of reduced volume fraction ϕ/ϕ_{max} for spherical suspensions. Curves B - E, reduced viscosity quantity $\eta_{sp}/(c[\eta])$ as a function of reduced concentration c/c_{cr} for γ polystyrene^{sample} in cyclohexane. Curves F and G the same as a function of reduced concentration c/γ , with $\gamma = 1$ for $M_n = 1.46 \times 10^5$. Position of F and G relative to other curves is therefore arbitrary.

Fig. 2. Reduced viscosity quantity as a function of reduced concentration c/γ for polyisobutene solutions. Ordinates displaced for two solvents.

Fig. 3. Molecular weight dependence of characteristic concentration γ and product $k_1[\eta]$ for polyisobutene solutions. The proportionality factor in eq. (2) is set equal to unity.

Fig. 4. Reduced viscosity quantity, eq. (1), as a function of reduced concentration for the polyvinyl chloride - cyclohexanone system. Insert, characteristic concentration factor and $k_1[\eta]$ as functions of M_v .

Fig. 5. Reduced viscosity quantity, eq. (1), as a function of reduced concentration for polyisobutene in xylene (I), and decalin (II). Arrows indicate locations of "entanglement" concentrations for particular molecular weights, calculated from ref. 39. Insert, characteristic concentration factor γ as a function of M_v .

Fig. 6. Reduced viscosity quantity, eq. (1), as a function of reduced concentration for polyisobutene in isooctane. Horizontal bar indicates range of reduced "entanglement" concentrations \tilde{c}_e , computed

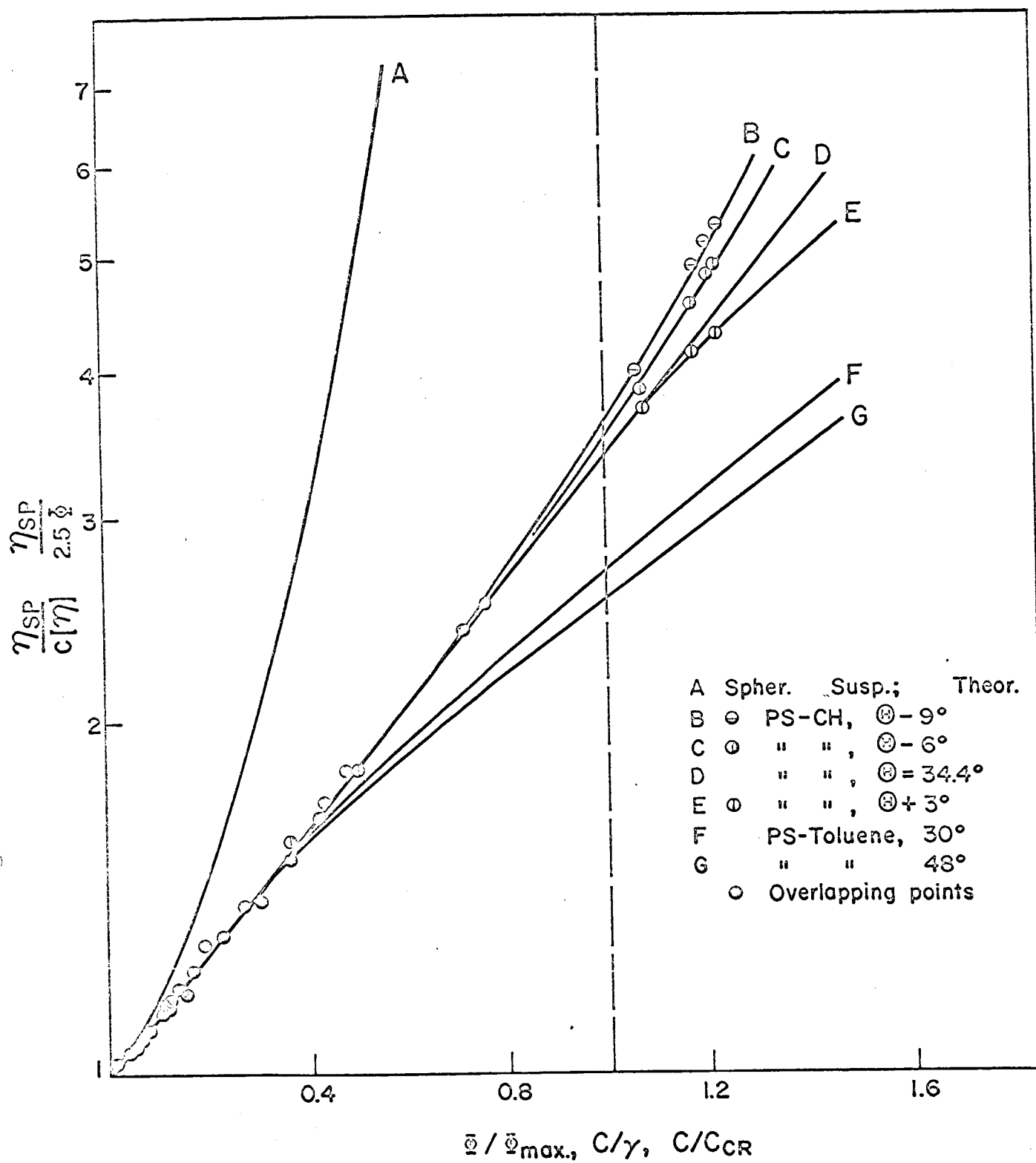
from ref. 9 and known γ . Insert, concentration factor γ and intrinsic viscosity as a function of M_v . Both are derived by superposition procedure.

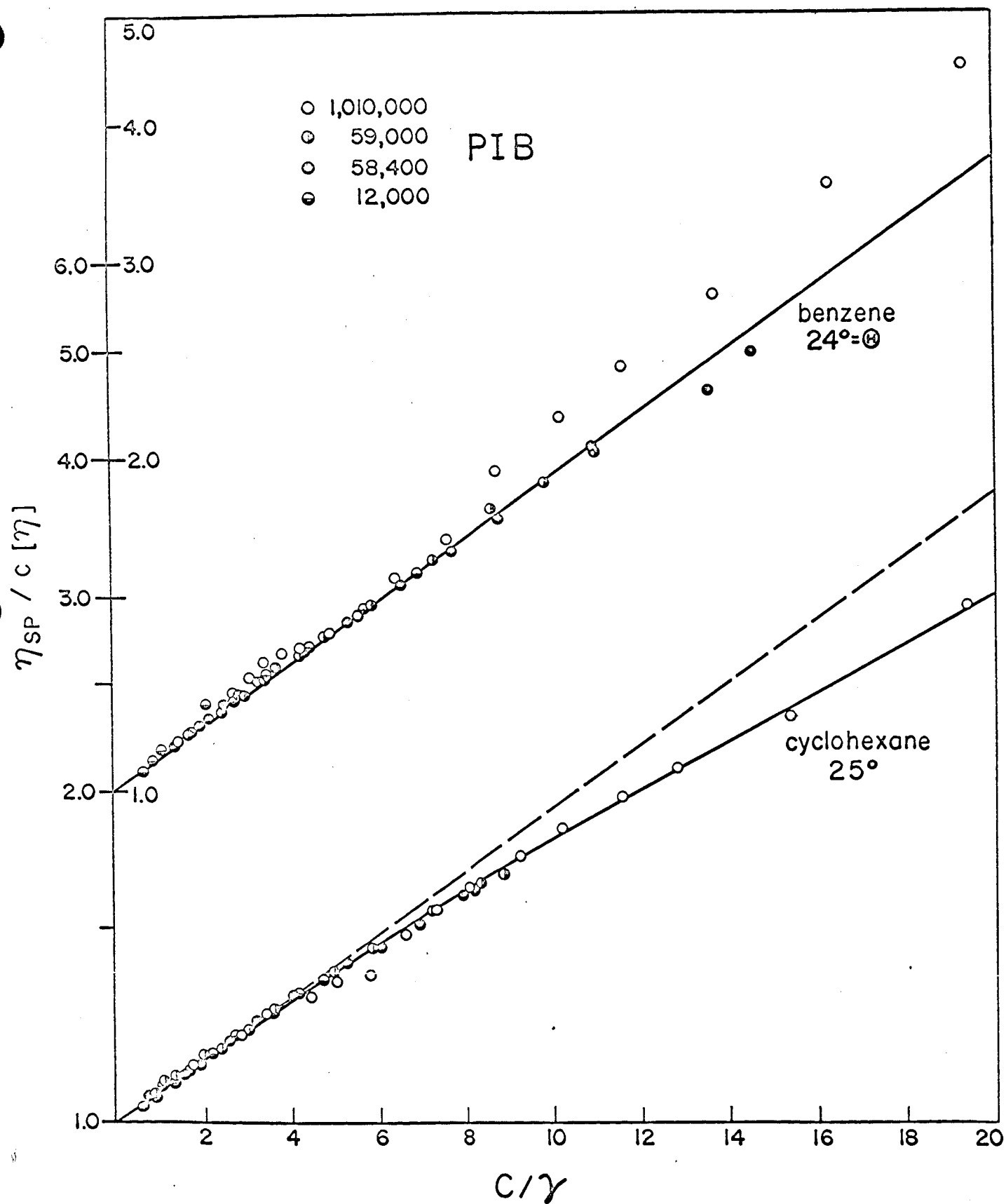
Fig. 7. Reduced viscosity quantity, eq. (1), as a function of reduced concentration for polyvinyl alcohol in water. No distinction between different molecular weights is shown. Horizontal bar indicates range of reduced "entanglement" concentrations \tilde{c}_e , computed from ref. 10 and known γ . Insert, characteristic concentration factor as a function of M_v .

Fig. 8. Reduced viscosity quantity, eq. (1), as a function of reduced concentration, for cellulose derivatives. Insert, characteristic concentration factor as a function of $[\eta]$.

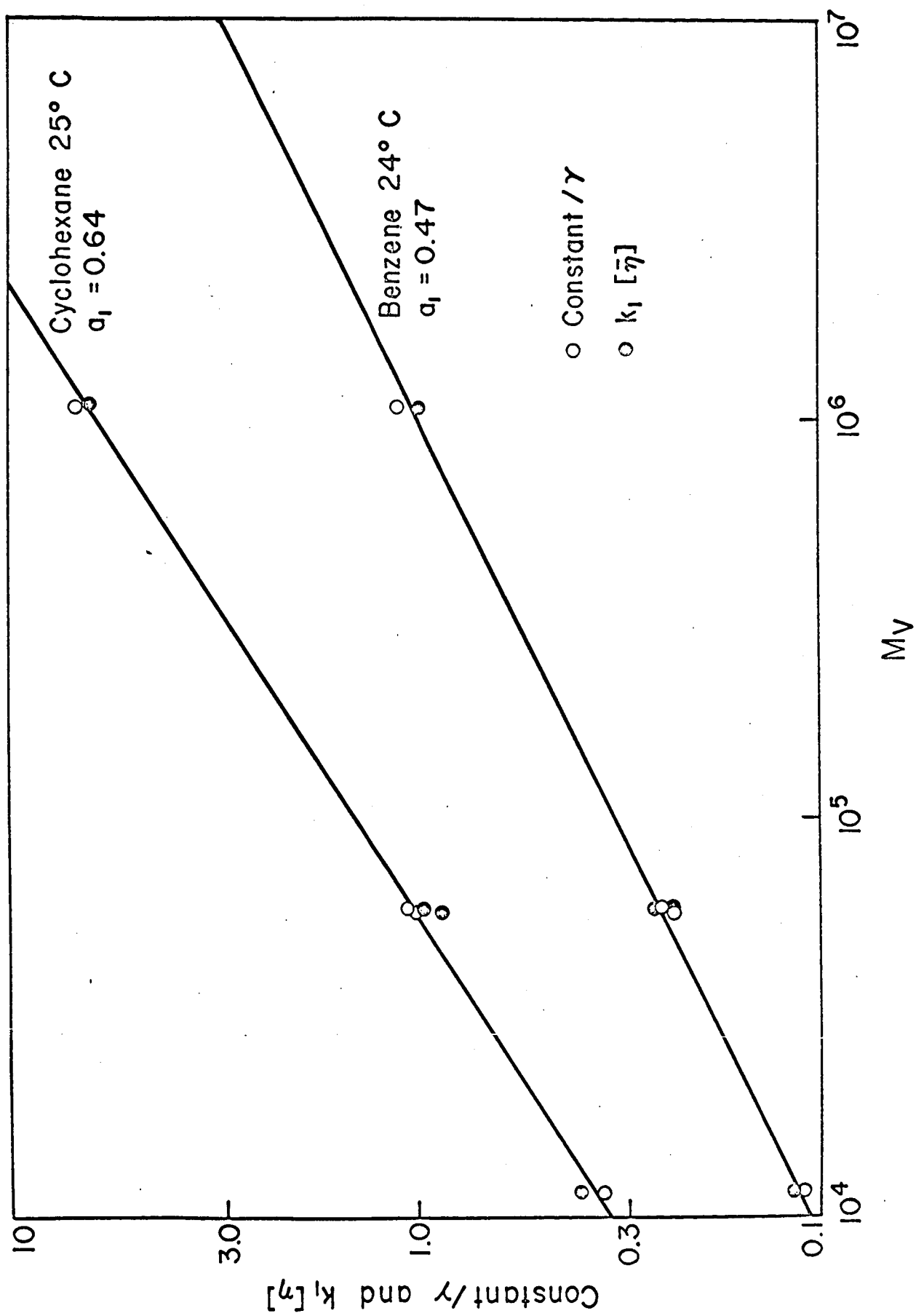
Fig. 9. Viscosity vs. molecular weight for the polyisoprene - decane system. The constant is chosen for each concentration so as to superimpose the three concentrations for $M_v < M_e$.

Fig. 10. Summary plot of reduced viscosity - concentration functions for polymers shown in Figs. 1 - 8 and for spherical suspensions. Relative horizontal displacements of curves 2 - 13 is arbitrary.

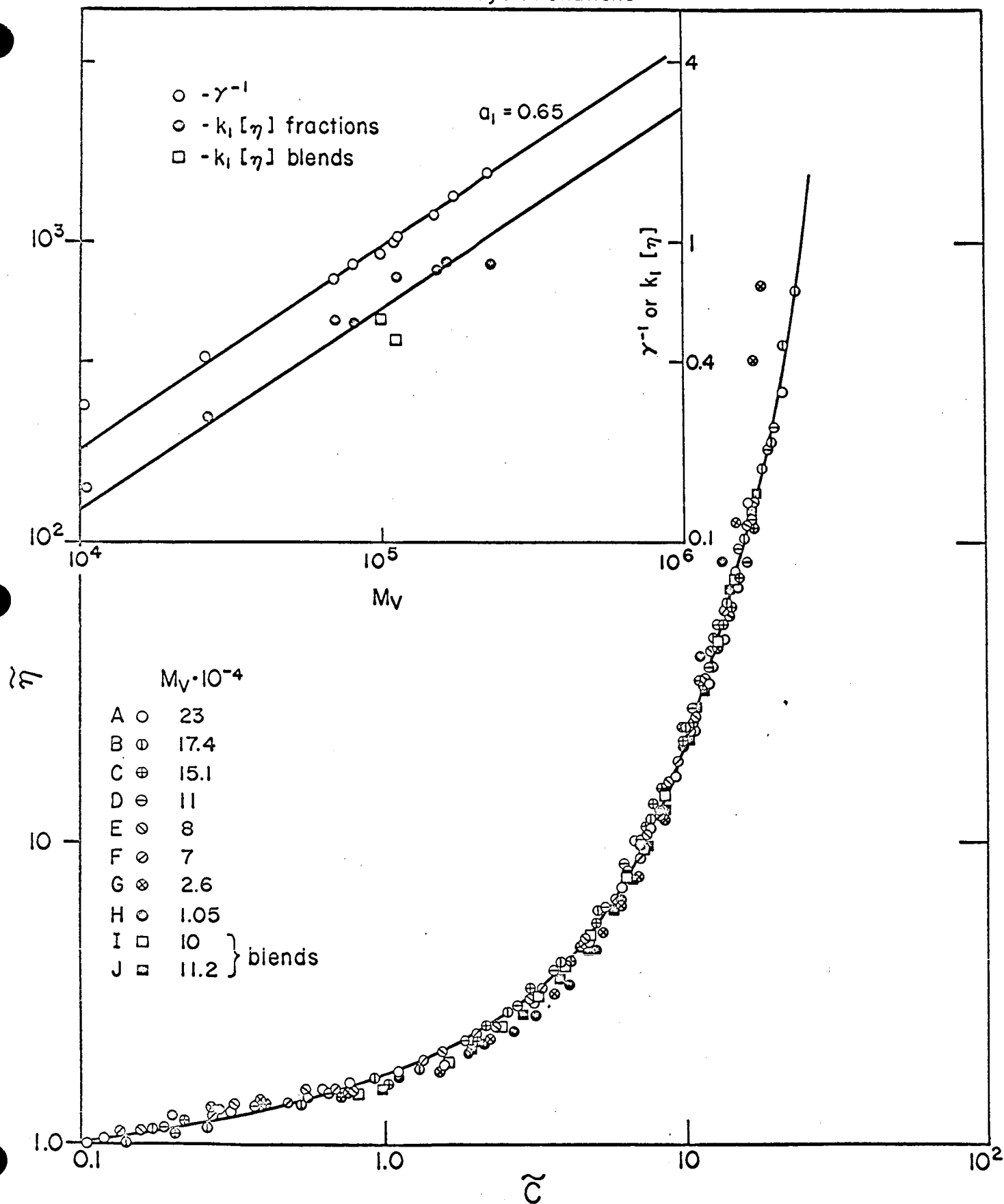


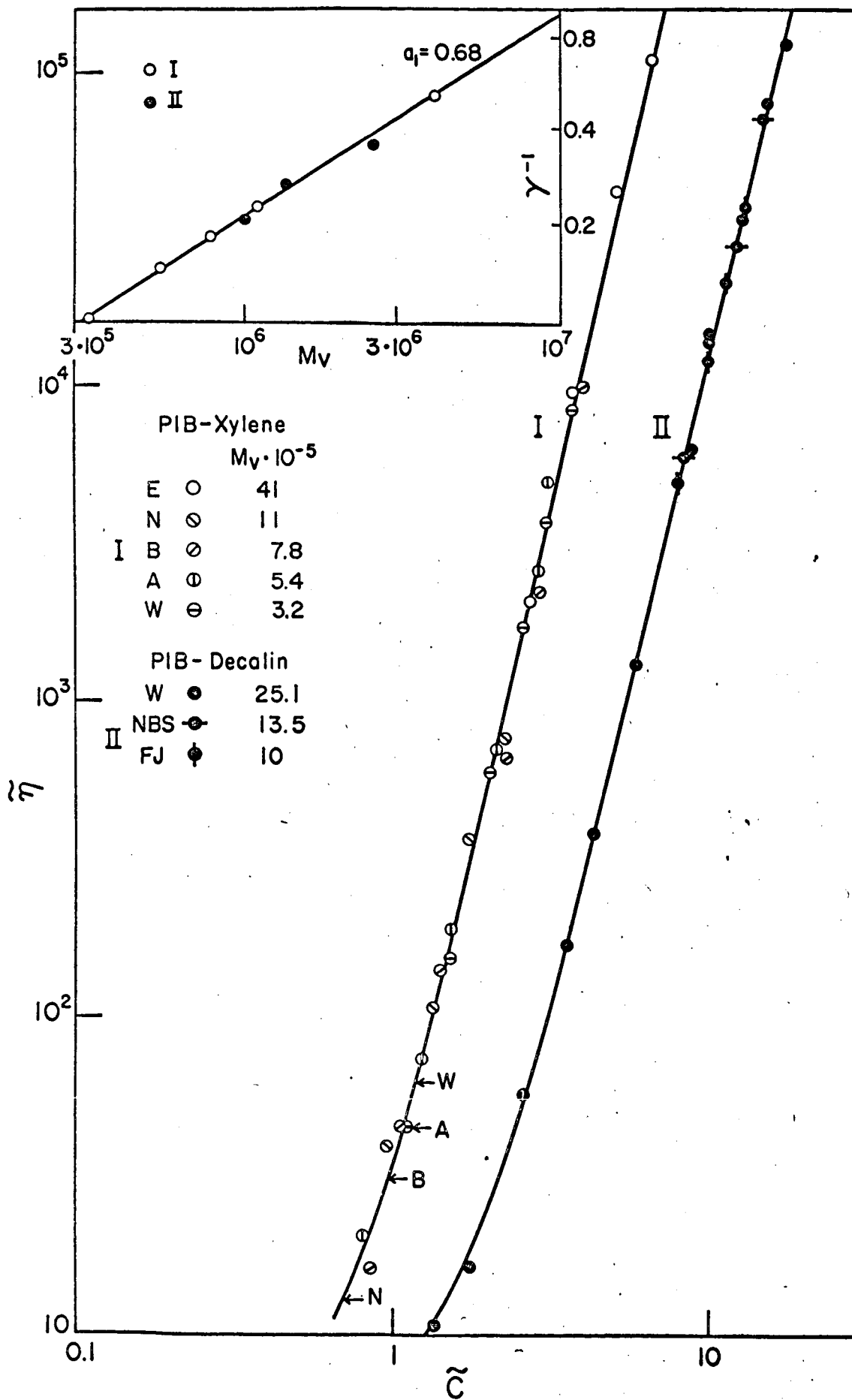


PIB

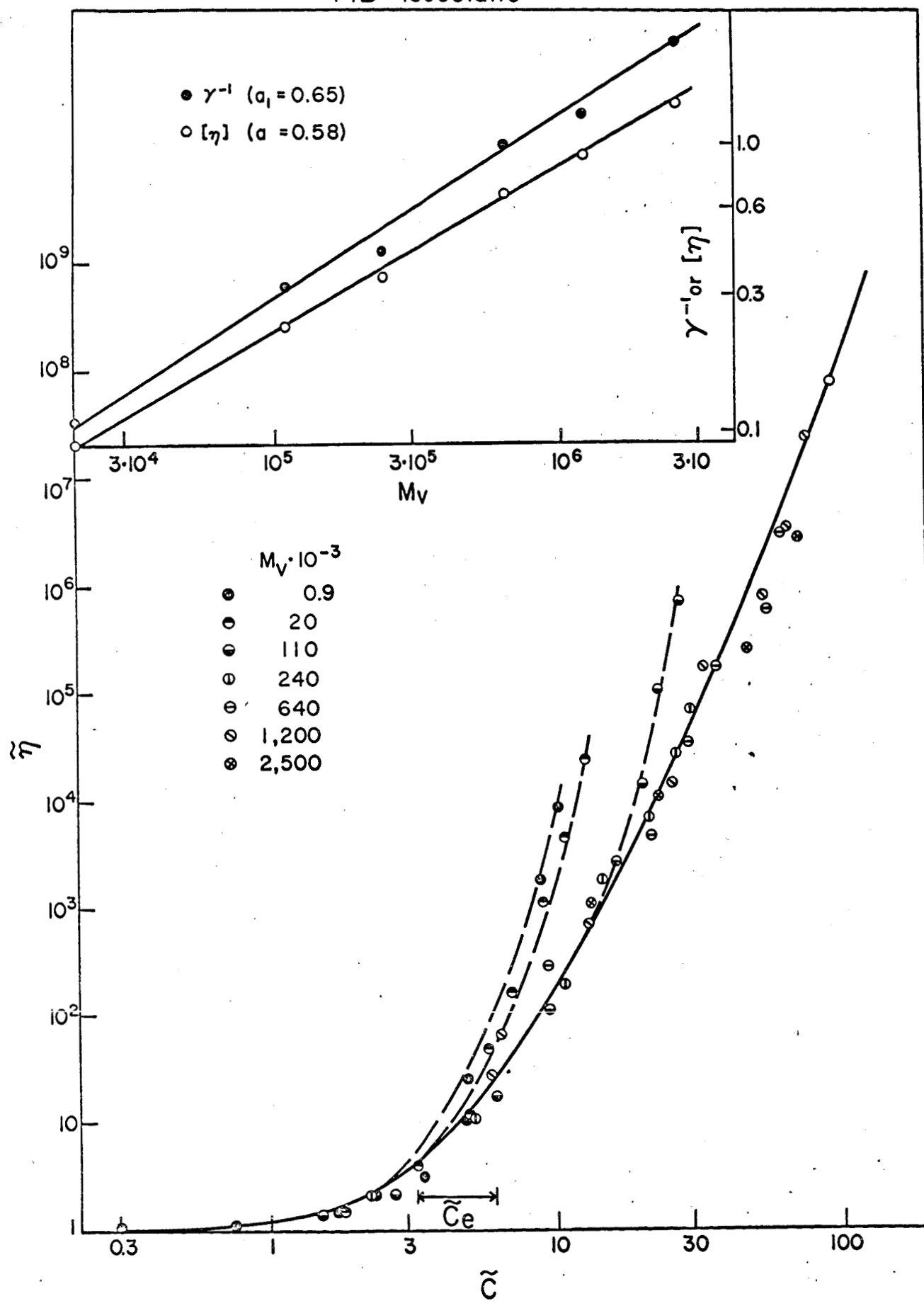


PVC - Cyclohexanone

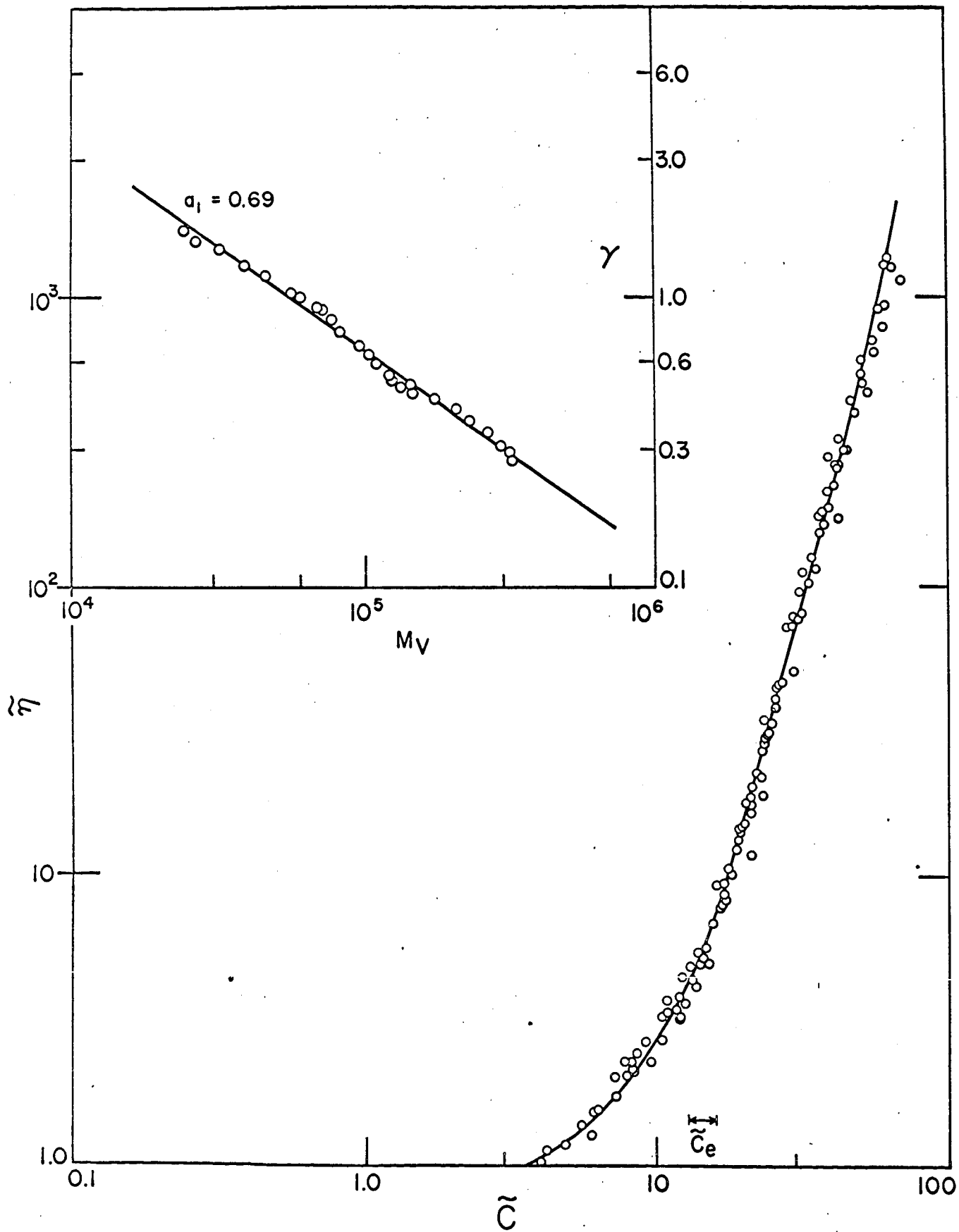


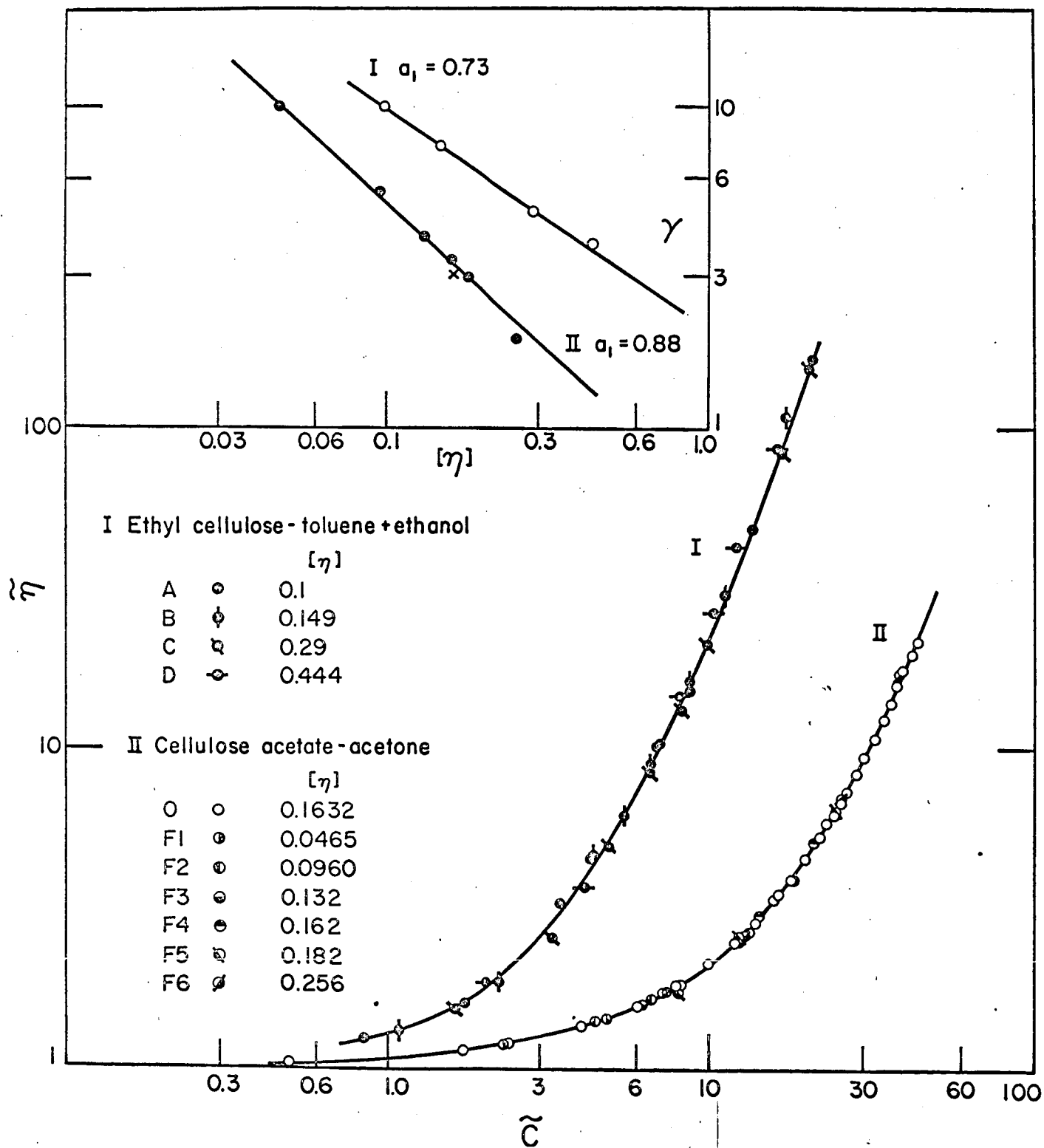


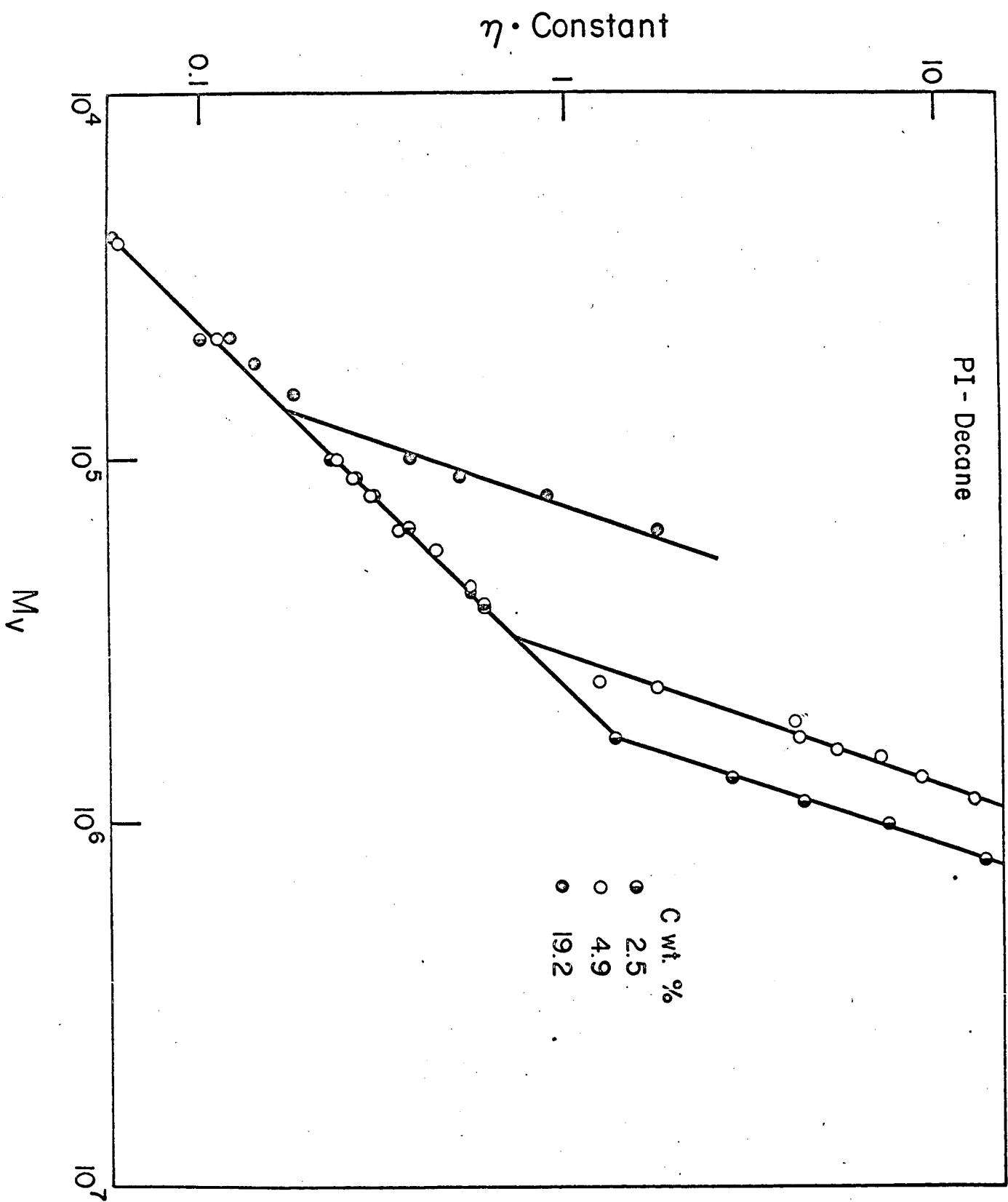
PIB- isooctane

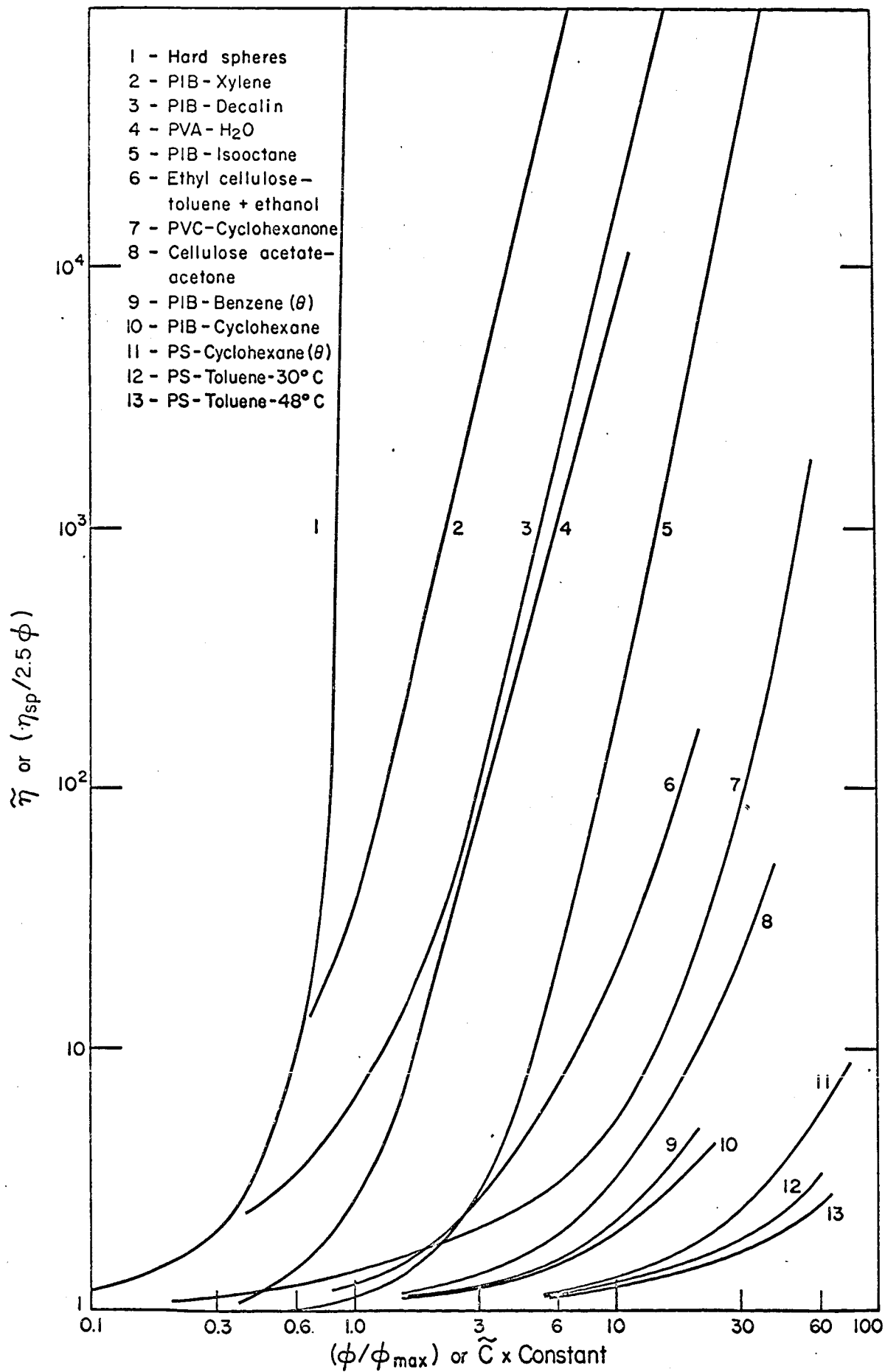


PVA - Water









MOLECULAR WEIGHT DEPENDENCE OF THE HUGGINS

CONSTANT k_1 AND THE PARAMETER γ .*

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SYNOPSIS

The theory of the Huggins constant k_1 has been developed on the basis of a theoretical viscosity - concentration relation for spherical suspensions and concentration dependence of the linear expansion factor $\alpha(c)$ of the polymer coil. Derived equations have been compared with the experimental k_1 values for 46 polymer-solvent systems. The molecular weight, solvent power, and permeability of polymer coil influences on k_1 are discussed. Through the simple relation between k_1 and the concentration reducing parameter γ , (from $\tilde{\eta}(c/\gamma)$ plots), developed equations predict equivalent dependences for γ as well.

INTRODUCTION

In previous papers^{1,2} we demonstrated the existence of a general, molecular weight independent function:

$$\eta_{sp}/c[\eta] = f(\tilde{c}) \quad (1)$$

where η_{sp} and $[\eta]$ are specific and intrinsic viscosities and $\tilde{c} = c/\gamma$ concentration and reduced concentration respectively. The reducing parameter

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γ for any system at constant temperature depends only on molecular weight (M) through a Mark-Houwink type equation:

$$[\eta] = K M^a; \quad \gamma = K_1 M^{-a_1} \quad (2)$$

Eq. (1) was found² to be valid for $0 \leq c \leq 50$ g/dl. The noted deviations occur for low M samples in a good solvent at higher concentration. For $c \rightarrow 0$ eq. (1) can be expanded into a power series:

$$\eta_{sp}/c[\eta] = 1 + m_1 c/\gamma + (m_2/2)(c/\gamma)^2 + \dots,$$

which by comparison with the Huggins eq.:

$$\eta_{sp}/c[\eta] = 1 + k_1[\eta]c + \dots \quad (3)$$

yields a very simple k_1 -M dependence:

$$k_1[\eta] = m_1/\gamma \quad \text{or} \quad k_1 = (m_1/KK_1)M^{a_1-a} \quad (4)$$

Previously³ eq. (4) was found to be valid for polystyrene (PS) - toluene and PS - cyclohexane systems.

Eq. (4) can be also used to calculate γ . This however demands a more thorough examination of the generality of the k_1 -M dependence. Furthermore, if $k_1[\eta]$ is taken as an experimental parameter $m_1 = \lim_{c \rightarrow 0} [\partial(\eta_{sp}/c[\eta])/\partial(c/\gamma)]$ still is not known. However if eq. (1) is general, independent of M, $m_1 \neq m_1(M)$. On this basis eqs. (1) and (4) permit the prediction of the viscosity of any sample of polymer in a wide range of concentration if the $\eta = \eta(c)$ of a single fraction and k_1 -M relations are known.

THEORY

To calculate theoretically the $k_1 = k_1(M)$ dependence we will proceed as

follows. If the eq.:

$$\eta_{sp} = 2.5\phi + 2.5^3\phi^2f^{-3} \quad (5)$$

developed by Sinha⁴ for hard sphere suspensions and recently checked by comparison with experiment⁵ should be valid for polymer solutions, then eqs. (3) and (5) must be equivalent and the volume fraction of the suspension, ϕ , can be expressed as follows:

$$\lim_{c \rightarrow 0} \phi/c = [\eta]/2.5 \quad \text{and} \quad \phi = [\eta](\alpha/\alpha_0)^{a^*}(c/2.5), \quad (6)$$

where α and α_0 are the linear expansion factors of polymer coil at concentration c and at infinite dilution respectively. The exponent a^* , from the relation

$$[\eta] = [\eta]_0 \alpha_0^{a^*}, \quad (7)$$

$$[\eta]_0 = 2.86 \times 10^{23} \cdot (6\langle s_\theta^2 \rangle)^{3/2} / M,$$

(where $\langle s_\theta^2 \rangle$ is the mean square radius of gyration), is assumed to be constant in the investigated range of concentration and for a given polymer solvent system. The theoretical⁶ a^* varies from 2.43 to 2.0, depending on the permeability of the polymer coil. Previously⁹ we found $a^* = 2.26$ for the PS - cyclohexane system, and this value will be used further in numerical calculations.

From eq. (3) we can define:

$$k_1[\eta]^2 \equiv \lim_{c \rightarrow 0} [\partial^2(\eta_{sp})/\partial c^2]_{M,T} / 2,$$

and using eqs. (5) and (6) we find:

$$k_1 = 2.5f_0^{-3} + (a^*/[\eta]) [\partial(\alpha/\alpha_0)/\partial c]_{M,T,c \rightarrow 0} \quad (8)$$

The first term in eq. (7) contains a packing factor f_0 at infinite dilu-

tion. The factor f^3 originally was derived⁴ from the assumption of the existence of an equivalent cage; the relation $f^3/\phi = R_h^3/R_p^3$ was established, which is valid for all concentrations (R_h and R_p are respectively the radius of an equivalent sphere and the radius of a particle). In other words, f_o^3 can be taken as a ratio of the hydrodynamic interaction volume (V_h) to the volume of the particle (V_p) at infinite dilution. For the hard sphere suspension, the theoretical value of f depends on the packing structure. For a hexagonal arrangement $f = 1.81$ (experimental value⁵ $f(\phi) \leq 1.85$ for $\phi \geq 10$ wt.%) and $f_o = 1.31 - 1.25$. Let us assume $V_h = [\eta]/2.5$ and V_p proportional to the sphere with the radius equal to the half of the longer axis of the polymer coil, visualized as a prolate ellipsoid. The second assumption will be justified in the discussion.

According to Kurata et al.⁶ the volume

$$V_p = (\pi N_A / 6) (\langle s_o^2 \rangle^{3/2} / M) (1 + 3\alpha_o^2)^{3/2} \quad (9)$$

Eq. (9) combined with eq. (7) leads to the relation:

$$f_o^3 = 13.33 \alpha_o^{2*} / (1 + 3\alpha_o^2)^{3/2} \quad (10)$$

which for $\alpha_o = 1$ gives $f_o = 1.19$. On the other hand, assuming that $1/\gamma$ is proportional to V_p and its value is determined by geometry of packing, i.e. $\gamma = 1/m_o V_p$, one can find

$$f_o^3 = m_o [\eta] \gamma / 2.5 \quad (10a)$$

where m_o is a numerical constant, dependent on the geometry of packing and permeability of the packed particles. For hard spheres in a face-centered cubic lattice $m_o = 2^{1/2}$.

To calculate the second term of eq. (8) we have to know the concentration

dependence of α .

A few years ago we showed⁷ that assuming a prolate ellipsoid model of a macromolecular coil whose volume changes with concentration under the influence of compressing energy, E , one can express $\alpha = \alpha(c)$ as

$$\alpha_0/\alpha = [(\alpha^2 - 1 + F_1 \tilde{c})/(\alpha_0^2 - 1)] [(1 + 1/3\alpha^2)/(1 + 1/3\alpha_0^2)]^{3/2} \quad (11)$$

where $F_1 \equiv [\partial(-E/RT)/\partial \ln \alpha]_{\tilde{c}}/3\tilde{c}$. For small concentrations, the relation can be simplified to

$$\alpha_0/\alpha = 1 + F\tilde{c} \quad (11a)$$

$$F = F_1(3\alpha_0^2 + 1)/(9\alpha_0^4 - 3\alpha_0^2 + 2)$$

Eq. (11) previously⁷ was checked for the PS-cyclohexane system at 30°C and 45°C. Taking F as a constant semiempirical factor, the equation was found to agree with experiments to much higher concentrations than expected ($c \leq c_{\text{crit.}}$). It is doubtful if this observation is general. However in the case of the present discussion of infinitely dilute solutions it is reasonable to assume $(\partial F/\partial \ln c)_{c \rightarrow 0} = 0$, which leads to:

$$-[\partial(\alpha/\alpha_0)/\partial c]_{c \rightarrow 0} = F_0/\gamma \quad (8a)$$

where $F_0 = \lim_{c \rightarrow 0} F$. Previous analysis⁷ of eq. (11) showed that the F_0 factor is slightly dependent on solvent power. The origin and nature of F_0 in this treatment was obscure.

It is very tempting to speculate on it. From eqs. (11) and (11a) it is evident that F_0 is a direct function of E . Let us consider one macromolecule in an infinite amount of solvent and the same macromolecule as increasingly more and more polymer is added to the system. The initial configuration corresponds to the α_0 expansion, the subsequent, to α . The configurational

changes ought to be governed by the excess free energy of mixing:

$\Delta F^E = n_1 \Delta F_1^E + n_2 \Delta F_2^E$. In the considered system (low concentration of polymer, at constant pressure and temperature), ΔF^E can be approximated by excess chemical potential of the solvent or by excess osmotic pressure

$$\Delta F^E \approx n_1 \Delta F_1^E \approx \Delta \mu_1^E = -V_1 \pi_2$$

where V_1 is a molar volume of the solvent and π_2 is excess or internal osmotic pressure, which can be conveniently expressed as a virial series:

$$\pi_2/RTc^2 = A_2 + A_3c + \dots$$

To calculate E from ΔF^E one has to notice that when E is energy per macromolecule, ΔF^E is energy of all polymer coils in the system, ergo:

$$E \approx n_1 \Delta F_1^E / n_2 \approx -n_1 V_1 \pi_2 / n_2$$

Expressing polymer concentration in the usual g/dl units:

$c \approx 10^{-2} n_2 M / n_1 V_1$ we can write

$$-E/RT \approx 10^{-2} A_2 M c (1 + c A_3 / A_2 + \dots) \quad (12)$$

Recently Berry⁸ showed that the expression:

$$A_2 = 4N_A \pi^{3/2} (105/134) \langle s_\theta^2 \rangle^{3/2} M^{-2} (\alpha_o^2 - 1) \quad (13)$$

is a good representation of the PS-solvent data in a wide range of temperature and M ($0.9 \leq \alpha_o^2 \leq 2.4$), predicting that it will be valid over the same range of variables for any flexible chain polymer in dilute solution. From eqs. (9), (11a), (12), and (13), assuming as above $\gamma = 1/m_o V_p$ we have

$$F_o = 0.2222 \alpha_o^2 / (3\alpha_o^2 + 1)^{1/2} (9\alpha_o^4 - 3\alpha_o^2 + 2) m_o \quad (14)$$

Substitution of eqs. (8a), (10a) and (14) into eq. (8) gives:

$$k_1(m_0[\eta] \gamma / 2.5^2) = 1 - \text{const. } F(\alpha_0)$$

$$\text{const.} = 0.2222 a^* / 2.5^2 \quad (15)$$

$$F(\alpha_0) = \alpha_0^2 / (3\alpha_0^2 + 1)^{1/2} (9\alpha_0^4 - 3\alpha_0^2 + 2)$$

Numerical analysis of $F(\alpha_0)$ shows that for the α_0^2 equals 1.0, 2.0, and 3.0 the function is respectively 0.062, 0.024, and 0.013. The numerical value of the const. in eq. (15) depends on the exponent a^* , i.e. on the permeability of polymer coils. It is worth noting that for the same polymer-solvent - temperature system $\alpha_0 = \alpha_0(M)$ does not change drastically. For $1 \leq \alpha_0 \leq 3$ one can find that⁸

$$(\partial \ln \alpha_0 / \partial \ln M)_T = (105/134) z / 4\alpha_0^2 \quad (16)$$

(where z is a known thermodynamical parameter), ergo the more drastic changes of α_0 can be expected in better solvents. However even in the PS - toluene system⁸ changes of M from 6.22×10^5 to 4.4×10^6 caused α_0^2 to change from 1.9 to 2.6. In other words, the change of $F(\alpha_0)$ due to the differences in M are small in comparison to the solvent power effects; k_1 should depend mostly on the second effect.

EXPERIMENTAL DATA

In figs. 1 and 2 typical plots of the product $k_1[\eta]$ vs. M are presented. In all 46 systems listed in Table I the linear double logarithmic relation predicted by eq. (2) was obtained and no systematic deviations were observed. From these plots the constants K_1 and exponents a_1 were calculated. (The additional reason for plotting $k_1[\eta]$ instead of k_1 was to avoid an accumulation

of experimental errors). The values of a vs. a_1 are shown in fig. 3. For systems 24, 31, and 32 (numbers refer to Table I), two values of a are listed; one given in the reference paper and the second (in brackets) calculated by us. The second value of a for the PVC system was determined by another author³⁴. Systems K1 - K7 were found to have constant values of $k_1 = 0.28 - 0.37$, depending on the system. Symbol N denotes those systems where the Martin equation is fulfilled.

DISCUSSION

The parameter γ in previous papers was shown to be proportional to the critical mixing concentration (c_{crit}) and/or entanglement concentration (c_e). In our method of superposition of viscosity data we were able to establish the exact values of a_1 . However K_1 always contained the disposable constant, the value of which depended only on the selection of reference M. In two cases we knew the molecular weight dependence of c_{crit} or c_e . Assuming those parameters to be numerically equal to γ , we were able to calculate K_1 and m_1 for those systems. For the PS- θ -solvent system (cyclohexane, 34.4°C), the value^{1,9} $m_1 = 1.18$ was found. For the polyvinyl alcohol - water system at 30°C, $c_e = 3.02 \times 10^3 M_v^{-0.693}$ was experimentally established. For this system k_1/m_1 for $M = 10^4$ and $M = 10^6$ was calculated as equal to 0.31 and 0.24 respectively. The experimental interpolated values for k_1 for these samples are 0.37 and 0.28, which lead to $m_1 = 1.18$.

The same value of m_1 found for poor and fairly good ($a = 0.64$) solvent systems may be taken as an experimental indication of insensitivity of m_1 to changes in α_o .

The theoretical value of m_1 can be calculated from eq. (15) if m_o is known. Its theoretical value of $2^{1/2}$ calculated for face centered cubic

lattice packing of hard spheres certainly cannot be applied to the polymer coil systems. Using the experimental value of $m_1 = 1.18$ we can calculate for PS- θ -solvent ($a^* = 2.26$): $m_0 = 5.263$. This high value of m_0 may indicate the elongation of polymer coils in accord with Kurata's initial assumption. The encompassed coil volume of a macromolecule cannot be impermeable to the segments of other polymer molecules. This leads to the conclusion that the "true" value of m_0 is even larger. On the other hand, interpenetration should increase with increasing the coil volume, i.e. with increasing the solvent power. These phenomena may be responsible for the relative stability of m_1 . At present it is impossible to predict its value in other than θ -solvent conditions. We have the evidence^{1,2} that m_1 is independent of M for each investigated system and that it slightly decreases with improvement of solvent. From eqs. (4) and (15):

$$m_1 \approx (2.5^2/m_0)(1 - 0.2222 a^* F(\alpha_0)/2.5^2) ;$$

if $m_1 \neq m_1(M)$, then the molecular weight dependence of $F(\alpha_0)$ must be compensated by m_0 and a^* changes. The last equation indicates also that even for the same solvent power we cannot expect the same values of m_1 due to possible differences in a^* . However it is worth noting that the contribution of the second "compressibility of a coil" term of the last relation is of the order of 0.4%. Then for practical reasons that relation can be simplified to the form

$$m_1 \approx 2.5^2/m_0 .$$

In fig. 4 the experimental values of $\log(KK_1/m_1)$ vs. $(a - a_1)$ are presented, from which the following relation is obtained:

$$KK_1/m_1 = \text{const.} (2.0 \times 10^5)^{a_1 - a}$$

Here the const. depends on the solvent power. With few exceptions for all systems with $a \leq 0.7$ the const. = 1.4. For systems with $a > 0.7$ no single value can be justified and $1.4 \leq \text{const.} \leq 3.0$. Introducing these empirical values into eq. (4) we obtain:

$$k_1 = (\text{const.})^{-1} (M/2 \times 10^5)^{a_1 - a} \quad (17)$$

From eq. (17) for $M = 2 \times 10^5$ the Huggins constant $k_1 = 0.71 - 0.33$, depending on the polymer-solvent system. It is worth noting that eqs. (8), (10) and (15) with the assumption $m_0 = 5.263$ and when changing α_0^2 from 1 to 3, i.e., changing solvent from θ to good solvent, predict a variation of k_1 from 0.79 to 0.26. The const. in eq. (17) must be proportional to m_1 , and good agreement between k_1 predicted from theoretical and calculated from empirical relations once more demonstrates the insensitivity of m_1 on solvent power. From a consideration of the packing of the polymer coils in the solution we have to deduce that not only the solvent power, but also the chemical structure of the polymer chain plays a role on m_0 and m_1 . A more extended coil, due to high polymer segment - solvent interaction or to the high stiffness of polymer chain, must cause an increase of m_0 and a decrease of m_1 parameter. This can explain the scatter of KK_1/m_1 values in fig. 4, for $a > 0.7$, and the impossibility of finding a single value for the const. in eq. (17) for these higher a 's.

Next let us discuss the M dependences of γ and $[\eta]$, i.e., the a vs. a_1 relation. In fig. 3 the experimental values of a vs. a_1 are plotted. As can be seen depending on the actual value of a , the difference $(a - a_1)$ can be positive, zero, or negative. In particular at $a = a_1 = 0.8$, i.e., in good solvent systems, the parameter f_0 must be independent of M and the symmetry of

hydrodynamic volume should be the same as the actual one. For these systems k_1 is independent of M .

The solid line in fig. 3 was calculated assuming $1/\gamma$ to be proportional to V_p and the validity of eqs. (7) and (9). Simple derivation leads to the eqs.:

$$a_1 = 1/2 + [9\alpha_o^2/(1 + 3\alpha_o^2)] \cdot (\partial \ln \alpha_o / \partial \ln M)_T \quad (18)$$

$$a = 1/2 + a^* (\partial \ln \alpha_o / \partial \ln M)_T$$

From eqs. (16) and (18) finally we have:

$$a_1 = a + \{[9\alpha_o^2/(1 + 3\alpha_o^2)] - a^*\} (\alpha_o^2 - 1)/4\alpha_o^2 \quad (18a)$$

As can be seen from fig. 3, eq. (18a) predicts a correct relationship between a and a_1 , which indicates that the assumptions leading to eq. (9) are justified.

Recently Zakin³⁷ established experimentally that for PIB and PS in good solvents the product $k_1 \alpha_o = \text{const.}$ Eq. (15) with $n_1 = \text{const.}$ fails to agree with this relation, due to too strong a dependence of α_o on γ ; for instance the change in α_o^2 from 2 to 2.5 gives a 20% increase in k_1 . On the other hand the empirical eq. (17) combined with eq. (18a) for⁸ $\alpha_o^2 = 1.9 - 2.6$ leads to: $k_1 = (1/1.4)(M/2.0 \times 10^5)^{-0.049 \pm 0.013}$. If Zakin's derivation is correct, then: $-(\partial \ln k_1 / \partial \ln M)_T = (\partial \ln \alpha_o / \partial \ln M)_T = 0.049 \pm 0.013$. From data of Berry⁸ the second derivative for the PS-toluene system varies from 0.04 to 0.08, which is in fairly good agreement with previous limits. It must be noted, however, that Zakin's equation can be applied only for the systems with $a \approx 0.6 - 0.7$. Systems with lower or higher values of the a -parameter will have different $k_1 = k_1(\alpha_o)$ relations.

Finally in fig. 5 the $k_1[\eta]$ vs. M_w data¹ for PS in toluene are presented.

The lines A, B, and C represent the same data plotted vs. M_n as in fig. 4 of the cited paper.¹ As expected the heterogeneity of the samples is almost excluded when the product k_1 is plotted vs. M_w .

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TABLE I

Viscosity characteristic parameters of infinitely dilute polymer solutions.

No. Polymer	Solvent	Temp. °C	M_w/M_n	a	$K \cdot 10^5$	a_1	K_K	No. of Samples	Ref.
1 Polystyrene	Toluene	25	>1.1	0.71	11.8	0.64*	10.8	22	1
2 "	"	30	"	0.72	9.2	0.64	14.9	9	1
3N "	Cyclohexane	34.4	1.05-1.8	0.50	0.902	0.47*	0.848	9	3
4N "	"	28	"	0.49	1.08	0.47	0.853	9	3
5 Polystyrene star branched	"	34.4	<1.1	0.496	86.9	0.532	35.96	12	10
6 "	Benzene	30	"	0.749	8.66	0.665	9.08	12	10
7 Polymethyl methacrylate	Acetone	25	fractions	0.70	7.5	0.69	5.61	6	11
8 "	Benzene	25	"	0.78	3.8	0.80	1.07	6	11
9 "	Chloroform	25	"	0.80	4.8	0.86	-----	6	11
10 "	Toluene	25	"	0.71	8.12	0.62	-----	6	11
11 "	n-amyl methyl ketone	25	"	0.65	-----	0.58	-----	6	11
12N Polyisobutene	Benzene	24	"	0.50	1.07	0.47*	-----	4	12
13 "	Cyclohexane	25	"	0.69	27	0.68*	-----	4	12

TABLE I (cont.)

No.	Polymer	Solvent	Temp. °C	M_w/M_n	α	$K \cdot 10^5$	a_1	K_K	No. of Samples	Ref.
14	Polyisobutene	Xylene	25	fractions	0.69	----	0.68*	----	5	13
15	"	Decalin	25	"	0.67	----	0.68*	----	3	13
16	Polyacenaphthylene	Benzene	25	~1.4	0.70	5.6	0.53	23.8	11	14, 15
17	"	Dichloroethane	30	~1.4	0.50	45.6	0.48	46.1	11	14, 15
18	Polycarbonate	Chloroform	20	~2.0	0.742	277	0.73	----	3	16
19	"	Tetrahydrofuran	20	~2.0	0.70	39.9	0.69	21.6	6	16, 17
20	"	Dichloroethylene	20	~2.0	0.82	11.1	0.74	12.3	7	16, 17
21	Poly(4 vinyl bis phenyl)	Benzene	25	~1.4	0.69	9.2	0.56	31.1	13	14
22	"	Dimethoxyethane	25	~1.4	0.53	37.0	0.46	62.5	13	14
23	Poly(isobutyl methacrylate)	Methyl ethyl ketone	25	fractions	0.70	8.61	0.88	0.16	6	18
24	Polyvinyl chloride	Cyclohexanone	30	"	0.86(0.77)	----	0.65*	----	10	19
25	Polyvinyl alcohol	Water	30	"	0.64	----	0.69*	----	27	20
26	Polyisoprene	Decane	25	~1.11	0.86	----	1.08*	----	12	21
27	Neoprene CG	Benzene	25	~1.9	0.89	2.02	1.03	0.144	12	22
28	Gutapercha	"	28	fractions	0.74	----	1.12	----	5	23

TABLE I (cont.)

No.	Polymer	Solvent	Temp. °C	M_w/M_n	α	$K \cdot 10^5$	a_1	K_K	No. of Samples	Ref.
29	Transisoprene	Benzene	28	1-2	0.65	43.7	0.84	-----	5	23
30	Polyundecanoates	Chloroform	25	1.94	0.93	6.9	1.08	0.488	6	24
31	3 nitro cellulose	Acetone	25	fractions	0.91(0.89)	11.0	1.00	2.0	32	25
32	"	Ethylacetate	25	"	1.03(0.91)	8.2	1.10	1.62	11	25
33	"	"	30	2.23	1.01	2.5	1.17	0.14	6	26
34	Hydroxy ethyl cellulose	Cadoxen	25	fractions	0.79	-----	0.73	-----	5	27
35	"	Water	25	"	0.87	-----	1.08	-----	5	27
36	Amylose	1/3 M KCl aq.	22.5	1.5	0.59	33.9	0.60	11.4	5	28
37	Polyvinyl pyrrolidone	10% NaCl aq.	25	1.64	0.70	14	0.64	9.7	10	29
K1	Poly α methyl styrene	Benzene	30	1.1	0.87	-----	0.87	-----	15	30
K2N	Polypropylene atact.	Decalin	135	fractions	0.80	-----	0.80	-----	4	31
K3	Poly(1-butene) isotact.	n-Nonane	35	2.26	0.80	-----	0.80	-----	8	32
K4	"	Ethylcyclohexane	70	2.26	0.80	-----	0.80	-----	8	32
K5	Polyacrylonitrile	Dimethylformamide	25	fractions	0.81	-----	0.81	-----	5	33

TABLE I (cont.)

No. Polymer	Solvent	Temp. °C	M_w/M_n	a	$K \cdot 10^5$	a_1	K_K	No. of Samples	Ref.
K6 Polymethyl methacrylate	Benzene	30	1.2-1.41	0.76	-----	0.76	-----	14	34
K7 "	Chloroform	30	"	0.80	-----	0.80	-----	14	34
BL1 Low density poly- ethylene resins	Wax	150	?	0.25	-----0.29-0.45	-----	-----		35
BL2 High density poly- ethylene resins	Wax	"	?	0.75-0.80	-----0.65±0.05	-----	-----		35

* a_1 determined from $1/\gamma$ vs. M and $k_1[\eta]$ vs. M plots.

$$K_K \equiv m_1 \cdot 10^5 / KK_1$$

M denotes systems where Martin equation is valid.

K denotes systems where k_1 's were found constant.

LEGENDS FOR FIGURES

Fig. 1. $k_1[\eta]$ vs. M for star branched polystyrene (curves 5, 6) and polycarbonate (curves 19, 20) solutions. Numbers refer to Table I.

Fig. 2. $k_1[\eta]$ vs. M for neoprene (curve 27), trinitro cellulose (curves 31, 32) and amylose (curve 36) solutions. Numbers refer to Table I.

Fig. 3. Exponent a vs. a_1 . Points are experimental; curve eq. (18a). Numbers refer to Table I.

Fig. 4. Semilogarithmic plot of (KK_1/m_1) vs. $(a - a_1)$. Numbers refer to Table I. Full circles represent systems where $a \leq 0.7$, empty circles represent systems where $a > 0.7$. Lines are drawn arbitrarily.

Fig. 5. Product $k_1[\eta]$ vs. M_w for PS in toluene at 30°C. Lines show $k_1[\eta]$ vs. M_n dependence¹ for the same set of experimental data separated into three ranges of heterogeneity.

20

19

6

5

 10^6 M_w 10^5 10^4 $k_1 [\eta]$

3

1.0

0.3

0.1

